

ELECTROCHEMISTRY  
OF  
ORGANIC COMPOUND

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BY  
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AUTHORIZED TRANSLATION FROM THE AUTHOR'S ENLARGED AND  
REVISED THIRD EDITION

OF  
ELECTROLYSIS AND ELECTROSYNTHESIS  
OF  
ORGANIC COMPOUNDS

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## AUTHOR'S PREFACE TO THE THIRD GERMAN EDITION.

THE great progress which the electrochemistry of organic compounds has made in the past few years rendered it desirable to rearrange the whole material, and to express by a suitable title the extension of the task which the book seeks to fulfil.

The theoretical discussions which form an introduction to the experimental part of electrolysis are of a subjective, partially hypothetical character, that the present state of our knowledge of the mechanism of the electrical reaction cannot prevent from being otherwise. But the given ideas have proved trustworthy as aids in directing and arranging my experimental work; perhaps they will be equally serviceable to others notwithstanding the possibility and justifiability of divergent views.

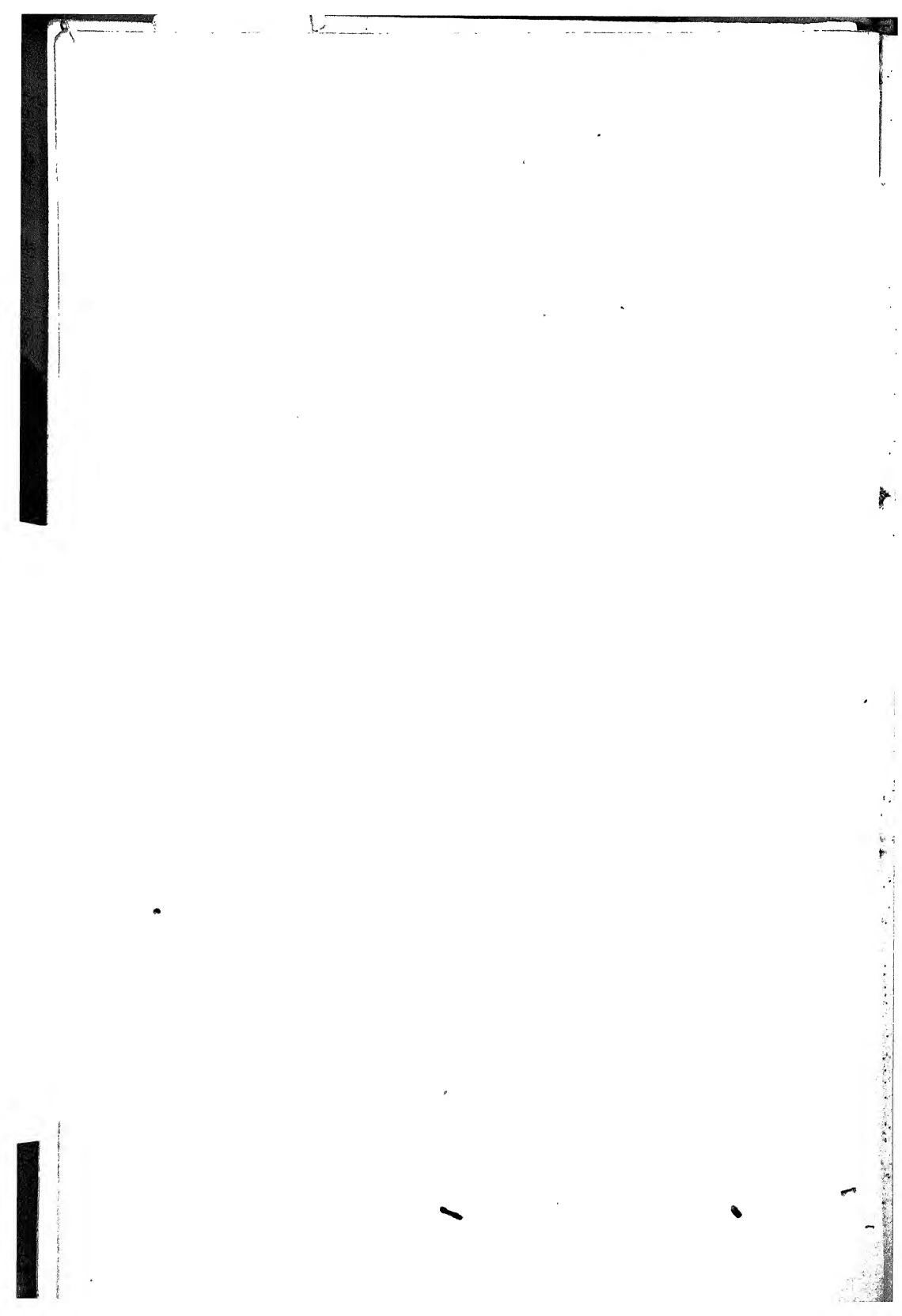
The object of the work has remained the same in the new as in the old form: to give a connected survey of what has been done, and to incite to further efforts in investigations.

I desire here to express my thanks to Dr. E. Gucke who helped me in looking over the literature on the subject.

The second English edition, corresponding to the present German edition, will appear shortly.

WALTER LENZ

Bonn, April, 1905.



## TRANSLATOR'S PREFACE TO SECOND AMERICAN EDITION.

A NEW edition of Doctor Löb's book on this interesting and important subject has become necessary, because of the great increase in the past few years in the quantity of new experimental material. The author has happily met this requirement in his present excellent work on the "Electrochemistry of Organic Compounds." Doctor Löb has spared no pains to bring the subject-matter strictly up to date, and has entirely rewritten and rearranged the material so as to present it in the best possible form.

Two special chapters have been arranged, devoted to a more thorough discussion of the theories and methodics of organic electrochemistry, and also a chapter on electric endosmose. The whole of Part II, on electrothermic processes and the silent electric discharge, is new.

Complying with the wish of the author in this as in the first translation, the original text has been followed by the translator as closely as possible.

It is hoped that this new edition will meet with the same cordial reception accorded the earlier one.

SPRINGFIELD, OHIO, October, 1905.



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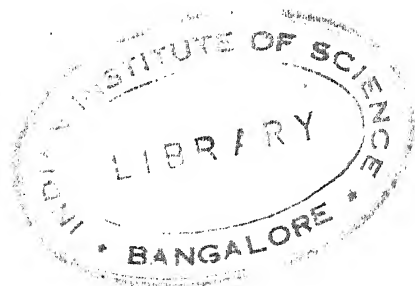
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# ELECTROCHEMISTRY OF ORGANIC COMPOUNDS.

## INTRODUCTION.

### CHARACTERISTICS AND CLASSIFICATION OF THE SUBJECT-MATTER.

THE application of electrical energy for effecting organic reactions was tried long ago and in the most various ways. The observations, however, were at first few in number, leading points of view were lacking, and the results were incoherent and often contradictory. A definite start in attacking the many problems which are presented by organic chemistry was not made until larger electrical equipments were introduced into scientific and technical enterprises. For about a decade organic electrochemistry has been undergoing a quiet but steady development.

Electrical energy can be employed directly or indirectly for accomplishing chemical reactions—directly, if the field traversed by the current is of an electrolytic nature; indirectly, if a transformation of electrical energy into other forms takes place, which—for instance, heat or light—can bring about chemical phenomena outside of the current field. Both utilizable forms of electricity are of theoretical and practical importance; the former in electrolysis, particularly in reduction, oxidation



and substitution reactions, the latter in pyrogenic and photochemical processes. Another kind of electrochemical action, and one in which the connection between electrical work and chemical effect is still hidden in obscurity, is the glow, or silent discharge. In spite of the few facts known about this form of electrical energy, it can be claimed positively that it is of fundamental importance in the synthesis of simple organic bodies and is, perhaps, a means for explaining the methods which living nature employs in building up substances.

A survey of the great number of organic electrochemical investigations shows a very unequal distribution of scientific labor among the separate parts of the extensive domain. The electrolytic reactions have been by far most thoroughly investigated, particularly the reduction processes. Oxidation and substitution reactions have more rarely been the subject of successful researches.

Pyrogenic decompositions and syntheses of organic substances produced by the induction spark, the electric arc, or highly heated conductors of the first class have been numerous mentioned. However, we are just beginning to obtain scientific results in this line of work. It has already been mentioned that our knowledge of the action of the glow and convective discharge on carbon compounds is extremely insignificant.

The varied properties of organic bodies explain this unequal treatment and the result. The reduction of carbon compounds occurs usually at certain reducible groups in the molecule without destroying this latter. The whole molecule is usually exposed to the action of the electrolytic oxygen. The final product of a reduction is closely related chemically to the material started out with; the end result of an oxidation is often the complete combustion of the molecule. Quite a number of possibilities exist between a slight attack by oxygen upon and the complete destruction of a compound by oxidation. A realization of these, if at all possible, depends upon most painstaking observations of fixed experimental conditions, which are often difficult to determine. Hence oxidation processes are much more com-

plicated than reduction processes, and usually less profitable. These same points of view also apply to electrolytic substitution, which, being an anodic process, is often only with difficulty protected from the oxidizing action of the current.

The relatively great sensitiveness of most carbon compounds to high temperatures confined electrothermic decompositions and syntheses of organic bodies to a small area, so long as the heat was derived from the induction spark, or the electric arc. Electrical energy has, however, proved itself a convenient medium for investigating the behavior of sensitive substances at relatively high temperatures, ever since metallic wires, or carbon filaments, have been used as sources of heat which can be easily regulated by increasing or decreasing the current pressure.

The properties of electric energy as well as those of the carbon compounds require special forms of experiment for organic electrochemistry. These differ entirely from the purely chemical art of experimentation, i.e., partially new experimental methodics are necessary. The more it was possible to recognize the important points in the course of an electrochemical process the clearer the viewpoints became regarding the choice of the most suitable conditions for experiment. The endeavor theoretically to represent and unite the numerous observations went hand in hand with the experimental development. Theoretical considerations led to new experimental conditions and new problems. The theory becomes closely associated, by certain requirements, not only with the subject of the experiment but also with its arrangement. A description of organic electrochemistry must fully recognize theory and methodics as well as the chemical results.

Depending upon the forms in which electrical energy is employed in organic chemistry, we can distinguish three processes, electrolytic, electrothermic, and electric-discharge reactions. A threefold division into theory, methodics and experimental results, hence, naturally follows for the disposition of each of the three resulting chapters.

It may be remarked, particularly in regard to the description of the methods, that only the necessary and important data are mentioned here. The author does not intend to give a practical guide for making experiments. Only original investigations or special text-books<sup>1</sup> can serve such a purpose. It is the object of the respective descriptions in this book to discuss the general principles and to lead the reader to a clear understanding and a correct interpretation of the various methods.

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<sup>1</sup> See, for instance, Oettel, *Electrochemical Experiments*, 1897 (translated by E. F. Smith); also Oettel, *Practical Exercises in Electrochemistry*, 1897 (translated by E. F. Smith, Phila.); Elbs, *Experiments for the Electrolytical Preparation of Chemical Preparations*, Halle, 1902.

# PART I.

## *ELECTROLYTIC PROCESSES.*

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### CHAPTER I.

#### THEORETICS.

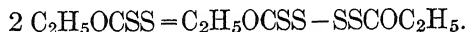
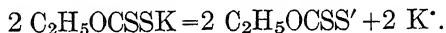
#### 1. FORMS OF REACTION.

Two possibilities must be distinguished in the electrolysis of organic bodies. The carbon compound is either an electrolyte, i.e., a salt, base, or acid, or it is a non-electrolyte.

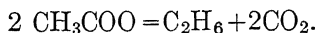
In the first case the compound itself furnishes the ions which condition the conductivity. The work of electrolysis then consists in the transportation of these ions to the anode and cathode, and it is a secondary question whether these ions are liberated molecularly or atomically, or whether they react with one another, or with the substance still present in the solution, or with the solvent.

Of the organic ions the anions are almost exclusively taken into consideration, since organic cations, like the organic ammonium ions, have been little investigated as to their behavior in electrolysis. The actual liberation of the ions cannot be observed, because when deprived of their electrical state they cannot exist. On the contrary, the anions often react with one another after their discharge. Thus either a union of several anions occurs or, far oftener, more complicated transpositions and decompositions accompany these reactions.

An example of the first kind of decomposition is furnished by the electrolysis of potassium xanthate<sup>1</sup>:



In this case two anions unite to form xanthic disulphide. On the other hand, in the electrolysis of sodium acetate, the anions are united, but carbonic acid is simultaneously split off:



The anions of the fatty acids show this behavior to a greater or less degree under certain current conditions.

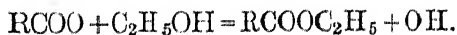
But if the organic compound does not conduct the current, other ions must be present for accomplishing the electrolysis. For this purpose usually an inorganic acid, base, or salt—corresponding organic compounds can of course also be used—is dissolved in the solution. Then, primarily, the passage of the current does not at all affect the organic non-electrolyte. Only the ions are driven to the electrodes where they can discharge themselves. At the instant, however, when the discharge occurs, the rôle of the organic body begins. If it cannot react with the discharged ions it remains unchanged, and is not affected by the action of the electrolysis. This possibility will naturally not be considered in the present discussion. The fact to be observed is, that the carbon compound reacts with the discharged ions—it then becomes a *depolarizer*.

Many organic acids, bases, and salts can act as depolarizers when ions are discharged which react easily with them. For example, p-nitrobenzoic acid in alkaline solution is reduced smoothly to p-azobenzoic acid. The sodium ions which are discharged react so rapidly with the nitro-group that the nitrobenzoic acid does not behave as an electrolyte but essentially as a depolarizer, particularly since the ions of the sodium

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<sup>1</sup> Schall, Ztschr. f. Elektrochemie 3, 83 (1896).

lution take care of the conductivity. Organic electrolites also furnish the ions which act upon an organic substance. Thus, if an acid is electrolyzed in absolute alcohol, sometimes formed:



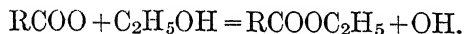
the alcohol is at the same time a solvent and a

we now divide the phenomena of electrolysis of carbon compounds into two classes: Either the organic bodies themselves are electrolytes—the effect of the electrolysis is the effect of the eventual additional reaction of their ions at the electrodes (primary reactions)—or they are depolarizers (secondary reactions).

The first class is by far the larger. It can again be subdivided into two groups, the cathodic and the anodic depolarizers. It is very seldom that a body acts simultaneously as a cathodic and anodic depolarizer. More often a cathodic depolarizer, by reacting with the cations (or anions), loses its faculty of now depolarizing anodically (or cathodically). For example, an easily reducible body may be reduced at the cathode into one easily oxidized, i.e. into one which acts as an anodic depolarizer. However, it is more clearness to adhere to the division into cathodic and anodic depolarizers and to determine the nature of the reactions.

**Depolarizers.**—Hydrogen and metal ions pass to the cathode. If we take no account of the small and unimportant organic cations. Hydrogen and metals can be reduced, i.e. deoxidized; and the hydrogen can also combine with the compound. Such bodies that can be reduced or take up hydrogen, or do both simultaneously, are called *reducible* compounds. They themselves are hence *cathodic* depolarizers. The characteristic property it is to destroy positive ions. The reaction at the cathode is called reduction. A cathodic depolarizer is reduced by the electrolysis.

hydroxide solution take care of the conductivity. Organic electrolytes can also furnish the ions which act upon an organic depolarizer. Thus, if an acid is electrolyzed in absolute alcohol an ester is sometimes formed:



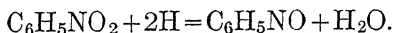
In this case the alcohol is at the same time a solvent and a depolarizer.

We therefore divide the phenomena of electrolysis of carbon compounds into two classes: Either the organic bodies themselves act as electrolytes—the effect of the electrolysis is the discharge and the eventual additional reaction of their ions at the electrodes (primary reactions)—or they are depolarizers (secondary reactions).

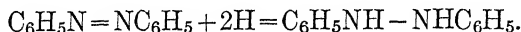
The latter class is by far the larger. It can again be subdivided into two groups, the cathodic and the anodic depolarizers. It is very seldom that a body acts simultaneously as a cathodic and anodic depolarizer. More often a cathodic (or anodic) depolarizer, by reacting with the cations (or anions), acquires the faculty of now depolarizing anodically (or cathodically). Thus, for example, an easily reducible body may be changed by cathodic reduction into one easily oxidized, i.e. accessible to the action of the anions. However, it is more conducive to clearness to adhere to the division into cathodic and anodic depolarizers and to determine the nature of the possible reactions.

**Cathodic Depolarizers.**—Hydrogen and metal ions pass to the cathode—if we take no account of the small and unimportant number of organic cations. Hydrogen and metals can withdraw oxygen, i.e. deoxidize; and the hydrogen can also be added directly to the compound. Such bodies that can yield oxygen or take up hydrogen, or do both simultaneously, are called *reducible* compounds. They themselves are hence oxidizers whose characteristic property it is to destroy positive discharges. The reaction at the cathode is called reduction. Every cathodic depolarizer is reduced by the electrolysis.

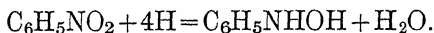
The reduction of nitrobenzene to nitrosobenzene furnishes an example of deoxidation:



In the conversion of azobenzene to hydrazobenzene an addition of hydrogen takes place:

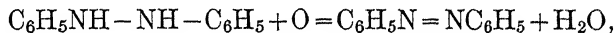


A withdrawal of oxygen and addition of hydrogen occurs simultaneously in the reduction of nitrobenzene to phenylhydroxylamine:

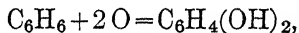


**Anodic Depolarizers.**—The conditions are somewhat more complicated at the anode. All the anodic depolarizers are oxidizable, it is true, even reducing substances which destroy the negative charges. But the reaction-picture is more varied at the anode than at the cathode—due to the individual variety of the anions. If the action consists merely in a withdrawal of hydrogen and an addition of oxygen, or both, it is called oxidation.

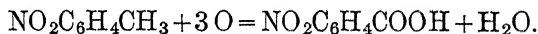
Examples of such oxidations are the conversion of hydrazobenzene into azobenzene:



the conversion of benzene into hydroquinone by a direct addition of oxygen:

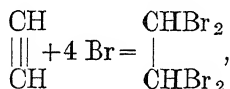


the production of nitrobenzoic acid from nitrotoluene by the addition of oxygen and withdrawal of hydrogen:

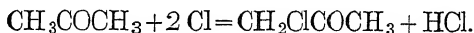




Discharged ions, like the halogens, are also often added directly to an organic, unsaturated body. An addition occurs, comparable with the addition of hydrogen at the cathode,



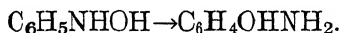
or, a substitution takes place, i.e. an anion—simple or compound—replaces an element or group of elements of the depolarizer,—e.g. in the electrolysis of acetone in hydrochloric acid:



Possibly the anion itself undergoes changes before it acts upon the depolarizer, so that the organic compound can no longer be spoken of as a true depolarizer for the anion but only for its decomposition products. Thus, in the presence of a base, the anion  $\text{CH}_3\text{COO}^-$  would behave in such a manner that, after it was split up into ethane and carbonic acid, only the latter would react with the base. However, such a reaction can no longer be regarded as an electrochemical one.

It seems particularly difficult to determine in a simple way the nature of an electrolytic reaction where there are so many possible ways for a reaction to take place. We shall see later on, however, that, by a proper consideration of the subject, a definition is obtained.

Another form of reaction occurs in the electrolysis of organic compounds. While it cannot be regarded as purely electrical, no more so than the preceding one, it appears only in a utilizable way among the peculiarities of the electrical method. The product resulting primarily, or secondarily, can occur first in an unstable modification, and can then rapidly undergo further changes. I shall here only refer to the intermediate formation of phenylhydroxylamine in the reduction of nitrobenzene in concentrated sulphuric acid, which, as is well known, immediately rearranges itself into amidophenol:



Gattermann<sup>1</sup> has shown that the unstable modification can be isolated by adding benzaldehyde to the original electrolytic fluid. The aldehyde reacts more rapidly with the intermediate product phenylhydroxylamine than the sulphuric acid can act to effect a molecular rearrangement.

Intermediate phases of electrical oxidation and reduction can similarly be isolated by adding to the electrolytes various substances which react more rapidly with the phase than the oxidation or reduction (regulable by the current conditions) can take place. This artifice, utilized by Löb<sup>2</sup> and Haber,<sup>3</sup> makes it possible to obtain theoretically important insights into the successive and often very transitory conditions of complicated processes.

## 2. PROPERTIES OF ELECTROLYTIC PROCESSES.

The electrolytic method possesses a number of properties which markedly distinguish it from all other chemical methods. In the first place the current produces the effect which the chemical method can accomplish only through the agency of certain materials, such as lead peroxide, chromic acid, etc., in the case of oxidations, and zinc, stannous chloride, iron, etc., in the presence of acids or alkalies in reductions. This effect is solely produced by ion-discharges, forces which are ultimately derived from a source of electrical energy, i.e. water power or coal.

A consumption of energy replaces a consumption of material. The economic ratio of these, which is of great practical importance, depends upon the factors controlling the prices of material and energy.

In such processes which require, even in electrolysis, the presence of certain substances endowed with characteristic oxidizing and reducing properties as a necessary component in the reaction, the actual material consumption is nevertheless very inconsiderable. The substances in question, for instance

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<sup>1</sup> Ber. d. deutsch. chem. Gesellsch. **29**, 3040 (1896).

<sup>2</sup> Ztschr. f. Elektrochemie **4**, 428 (1898).

<sup>3</sup> Ibid., 506 (1898).

the metallic salts, need only be present in the electrolyte in very trifling quantity, since, after accomplishing their purpose they are regenerated by the current and can be reused for accomplishing innumerable reactions. In this case, also, only the question of energy need be considered.

Moreover, the electrochemical method allows the confining of the reaction to a certain space within the chemical system. The reaction occurs only in the immediate neighborhood of the electrode,—thus the reactions of the ions themselves take place on the electrode surface at the instant of their discharge, those of the depolarizers in proportion to the quantity coming in contact with the electrode surface, either by diffusion or stirring. The extent of the space in which the reaction occurs therefore depends upon the extent of the electrode surface; it can be considered as an extremely thin layer which is in intimate contact with the electrode. In this layer the reaction processes occur in accordance with the known laws of reaction kinetics, i.e. their velocity depends upon the concentration of the active molecules. These are, however, the ions just discharged, either alone, when they react with one another, or simultaneously with the molecules of the depolarizer. The concentration of the latter is independent of the electrical conditions, but the concentration of the ions is determined by the intensity of the current, according to Faraday's law.

### 3. SIGNIFICANCE OF THE VELOCITY OF REACTION.

The electrically feasible reaction conditions are (1) the extent of the reaction space and (2) the quantity of reactive ions in the latter, i.e. the concentration of the ions can be regulated in a purely electrical way and within the broadest limits. The highest dilutions can be realized just as well with weak currents and large electrode surfaces as the highest concentrations with strong currents and small surfaces. That most important factor of reaction kinetics, the *reaction velocity*, is thus determinatively influenced by these concentrations. The importance of the reaction velocity is especially fundamen-

tal for the course of the reaction; for in the majority of cases it is a case of processes vying with one another, the reaction velocities of which determine the preponderance, and hence the result, of the one or the other process.

The last remark, that competitive reactions occur almost always, needs a brief explanation. One reaction possibility is electrolytically always present—the liberation of the ions in a molecular state on the electrode. This liberation is a reaction which must not be confounded with the discharge which precedes it. The discharge takes place in accordance with Faraday's law, and since the discharged ions—they are either atoms or "unsaturated" groups formed by dissociation—cannot exist, they react with a certain but unknown velocity. They thus combine to form molecules or complexes, and the stable end-products are liberated in conformity with Faraday's law, the quantity separated being proportional to the discharge. But if a depolarizer is present, the discharged ions have the opportunity to react with it instead of being set free. The depolarization reaction also takes place with a certain velocity. The two velocities, however, are decisive for the partitive ratio between an ionic liberation and a reaction with the depolarizer. Herein lies the importance of reaction velocities in electrolytic processes.

The question follows: How can we regulate *ad libitum* these velocities, i.e. usually make the reaction with the depolarizer the most predominating one? Apparently this is only possible within the bounds set by the chemical nature of the active molecules—by a shifting of concentrations in the reaction space, which can be regulated on the one hand by the variation in the quantity of the depolarizer, and on the other hand by the concentration of the discharged ions and the size of the reaction space, i.e. the electrode surface. The velocity of liberation is also increased by increasing the current strength, upon which the prevailing concentration of the discharged ions in the unit of time depends, likewise by decreasing the electrode surface, which has the same effect as the increase in concentration. It will therefore be the experimental problem

to choose the current strength, electrode dimension, and depolarizer quantity in such a manner as to produce the desired effect.

The ratio of the current strength to the electrode surface is called current density. This latter and the quantity of the depolarizer therefore are decisive factors in electrolysis.

#### 4. REACTION VELOCITY AND SPECIFIC EFFECT OF REDUCING AND OXIDIZING AGENTS.

These conditions can only give an insight into the quantitative course of an electrolysis. The qualitative course of the reaction is conditioned by the chemical forces of affinity specific of the single elements or compounds and characteristic of the reacting masses.

In the majority of the electrolyses of organic bodies the circumstances are very much simplified by the fact that it is only a question of two different forms of reaction, viz. reduction and oxidation. The limits within which a reduction can take place at all are already given in the case of a cathodic depolarizer by its nature, no matter which reducing agent is employed. For instance, only nitrosobenzene, phenylhydroxylamine and aniline need be considered in the reduction of nitrobenzene, and the chemical nature of the reducing ions cannot enlarge these boundaries. Since the single reduction phases are quantitatively related to one another, the one following being always the direct reduction product of the preceding one, and since the obtainable phase depends solely upon the more or less strong reduction, the special efficacy of the various reducing agents presents itself as a quantitative order which can be repeated at will. The individual properties of the reducing agencies become mutually comparable in a quantitative way. For instance, if nitrobenzene is reduced to aniline with copper and sodium hydrate, but, using zinc and sodium hydrate solution, only to azobenzene, the specific action of the copper and zinc is shown qualitatively, but the quantitative connection exists also at the same time that copper is a stronger reducing agent than zinc, i.e. a qualitatively equal agent.

The effects producible by choosing a suitable reducing agent can also be obtained electrically. The important problem arising in electrolysis is to convert the qualitative phenomena into quantitative ones, and to find a uniform measure for the changing effects. Naturally, the above applies in like manner to an oxidizing agent.

As we have already seen, the current density is the regulator of the electrically obtainable concentration conditions for the discharged ions, and thereby becomes codeterminative of the velocity of reaction. The obtainable phase of an oxidation or reduction is intimately related to the velocity of reaction, for as soon as the reaction velocity of the liberation of reducing or oxidizing ions greatly exceeds the reduction or oxidation velocity with the depolarizer, the reduction or oxidation stops. Thus the obtainable phase, i.e. the quality of the reaction, occurs also as a function of the reaction velocity.

##### 5. ELECTRODE POTENTIAL AND REACTION MECHANISM.

The question touched upon above can be more fully defined as follows: Do we know of a factor which includes both the concentration conditions at the electrodes—the functions of the current density and depolarizer concentration—and also takes into consideration the individual character of the active masses,<sup>1</sup> i.e. the ions of the depolarizer? The answer is affirmative. All these influences are contained in the electrode potential.

This claim becomes intelligible if we consider more carefully the nature of the electrode material. It is necessary to choose a certain theory among the various ones which have been proposed—with more or less justification—on the electrical mechanism of reaction. I select that one which seems to me to have the best foundation. The fundamental idea of this theory has been derived from Tafel.<sup>2</sup> Its general usefulness

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<sup>1</sup> The nature and the efficacy of the electrode metal are included in the term of "active masses", the ions. This will be shown below.

<sup>2</sup> Ztschr. f. phys. Chemie **34**, 199 (1900).

I<sup>1</sup> have explained in conjunction with R. W. Moore. The whole idea will be here predicated and developed.

Without laying too much stress upon the most modern view, that of regarding electricity atomically by means of the idea of electrons, all known phenomena justify us in dealing with positive and negative electrical quantities as with chemically active masses, and applying to them the principles of reaction kinetics.

The ions are accordingly chemical compounds, so to speak, of atoms and electrons.

The process in an electrolysis is the following: The ions migrate to the electrodes, the cations to the cathode and the anions to the anode. This takes place as soon as they come within such proximity of the electrodes that a neutralization of the electricity can occur. We are justified in assuming that this phenomenon takes place on the border line between the metal and the solution in such a manner that the ions touch the electrode, strike against it, but without being on the electrode; the discharge of the ions will occur in an extremely thin layer immediately above the surface of the electrode. In the case of elementary ions, this discharging process yields free elementary atoms of great affinity; complex ions give very reactive groups which are unsaturated and possess "free" valences, and hence are very prone to react further.

The supposition of such a discharge which precedes the deposition is not arbitrary, but necessary. The supposition that the discharge does not take place on the electrodes but at the latter, seems at first somewhat arbitrary. However, the behavior of attackable cathodes proves conclusively that the discharge cannot occur on the electrode. We also arrive at formulae which conform to the observations, if we suppose that the discharged but not yet liberated ions obey the laws of osmotic pressure, i.e. the laws governing gases. This fact seems clear, and agrees with our knowledge of the matter, if the discharged ions are in a liquid layer, no matter how thin

<sup>1</sup> Ztschr. f. phys. Chemie 47, 418 (1904).

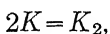
this may be. It is very difficult to understand, if the ions discharge themselves upon the metal surface. We would then be compelled to assume that the solution of any atoms in solid metals obeyed the laws of gases, an assumption which is very improbable and leads, especially in anodic phenomena, to impossible consequences.

The gist of this view is the strict division of the electrode process into the ionic discharge, by which the ions are transferred into the atomistic or unsaturated (very reactable) state, and into the molecular separation of the discharged ions. This second process takes place with a certain velocity the true value of which is unknown to us. It is in general so rapid that discharge and separation appear to us to occur simultaneously. The discharge takes place according to Faraday's law; likewise the separation, after a stationary equilibrium prevails between the discharged ions, the atoms or unsaturated groups, and the separation products.

We can write the first process as a cathodic reaction:



the second as



whereby the second equation may be perhaps reversible, as above mentioned. Accordingly, apparent divergences from Faraday's laws may occur at the beginning of the electrolysis.

If we also assume the first equation as reversible, the participation of the electrolytic osmotic pressure would follow from simple reaction-kinetic considerations.

The second equation is of more interest here. It takes place evidently with a finite velocity so that other velocities can compete with it. This last is afforded by the reaction of the discharged ions with the depolarizer. When this velocity is far the most important one a separation of ions cannot be observed; as is the case with many oxidations and reductions.

Chemical work, with which a certain amount of heat and external work (increase in volume, overcoming pressure) is



often associated, is done at the electrodes. The total work in electrolysis is supplied from the electric energy, i.e. the product of potential and the quantity of electricity. The quantity of electricity necessary for the discharging of a gram-equivalent of ions is always the same in accordance drawn from Faraday's laws. Therefore the total work accomplished by a gram-equivalent of ions, i.e. the sum of chemical work, external work and possibly liberated heat, must be proportional to the electrode potential. If the electrode process consists only of a chemical reaction, in a change of the internal energy of the reacting system, the potential must necessarily be determinative for the value of the work of this change. It is, of course, an entirely different question as to what chemical products are formed. The chemically individual character of the reacting bodies comes into play here, the known fact that the end-product of a reaction—irrespective of the value of the energy change taking place—is chemically always more or less related to the materials started out with. The sequence of these considerations is that equal potentials can produce only like *dynamic* effects.

If the potential is expressed by the Nernst formula,

$$E = \frac{RT}{F} \ln \frac{c_1}{c_2},$$

in which  $c_1$  is the concentration of the discharged ions which, obeying the laws of gases, seek to re-enter the electrolyte with a certain pressure—the electrolytic osmotic pressure—and  $c_2$  is the concentration of the ions in the electrolyte, it is very evident that the potential must contain, apart from the ionic concentration of the electrolyte, all influences which determine the concentration of the discharged ions ( $c_1$ ). These influences are, primarily, the current density whose size regulates the number of the ions discharged in a unit of time at a given electrode surface, hence regulating its concentration; secondarily, the reactions of the ions with one another and with the depolarizer. For variations in the concentration of the value

$c_1$  occur through both processes and, since the velocity of the reaction of the discharged ions with the depolarizer also depends upon its chemical nature and concentration, these two last-mentioned factors are also embraced by the potential.

A more thorough knowledge of these relations is gained by a consideration of the typical electrode processes.

## 6. ELECTRODE PROCESSES.

### A. Cathodic Processes.

#### *a. Unattackable and Attackable Cathodes.*

In organic chemistry only those cathode processes are of importance which occur with the reduction of an organic depolarizer. This reduction is done by the ions discharged at the cathode. The chemical nature of these ions can be very variable and, conjointly therewith, the reduction can occur in a variable manner.

In acid solution—assuming the depolarizer to be a non-electrolyte—hydrogen ions will occur, and in alkaline solutions alkali ions, and by making suitable additions any desired kind of ions can be brought into action at the cathode; thus any metal ions may be set free. The metal ions are either added directly to the electrolyte in the form of a metallic salt or hydroxide, or they are derived from the cathode metal itself, in case the cathode is "attackable", and pass from this into the electrolyte.

The various reduction processes can be brought about simply if the cathode metal is primarily considered and a distinction is made between attackable and unattackable cathodes. The former are such as give no active ions in the presence of the respective electrolyte and depolarizer, so that only the cations of the electrolyte can be shown to be discharged by the current. Attackable cathodes are those which send traceable quantities of ions into the electrolyte during the passage of the current, or in its absence. Naturally, only those attackable cathodes which can yield reducing ions are of interest here.

Since some investigators seem to believe that every reduc-

tion must be referred to the action of hydrogen, let it be emphatically pointed out here that, besides many chemical phenomena, the fact that it is immaterial whether the reduction is made at an attackable cathode or by the addition of the ions of this cathode metal to the electrolyte at an unattackable electrode proves the reducing capacity of the metal. In both cases similar results are obtained. But if ions of attackable metals are added, this metal is not deposited on an unattackable electrode so long as sufficient quantities of the depolarizer are present and the velocity of depolarization sufficiently outweighs the velocity of discharge. Although the cathode metal, say platinum, always remains the same, an effect occurs nevertheless, similar to that which would be obtained at a cathode composed of the attackable metal in the electrolyte. The conclusion follows necessarily that these metal ions in the electrolyte, and not the hydrogen atoms, determine the reducing action by their separation on or in the electrode.

We can hence consider conjointly the case of attackable electrodes with that of the presence of metal ions in the electrolyte at unattackable electrodes, and contrast this with the reduction by hydrogen at unattackable electrodes.

For the latter we will suppose that the hydrogen atoms discharge themselves in the cathode boundary surface, and that these discharged ions have two reaction possibilities at their disposal. They are either separated molecularly on the cathode, or they reduce the depolarizer. The reduction velocities of both processes are determinative for the ratio of division. If the reduction takes place far more quickly than the formation of hydrogen molecules, practically no hydrogen will be evolved. The velocity of hydrogen formation is hence of importance in the utilization of the current action for reduction. It depends to a great degree upon the chemical nature and surface condition of the cathode, and is very likely related to the catalytic nature of the metal. These phenomena will be considered conjointly under the discussion on "excess potential."

Ions are sent off from attackable cathodes immediately into the electrolyte, so that the relations in the latter are qualita-

tively the same as when metal ions are added directly to the electrolyte. The metal employed as cathode is hence immaterial for the effect so far as it has not actually reacted with the electrolyte, and can often be replaced by an unattackable cathode.

Under these conditions the metal ions play the rôle of hydrogen atoms, as above explained. They discharge themselves in the cathode boundary surface and, depending upon their reaction velocities, affect the reduction of the depolarizer and the metallic deposition. With a great reduction velocity, therefore, no metal whatever is deposited on the cathode so long as sufficient quantities of the depolarizer are present.<sup>1</sup>

An important result of these considerations, and one which confirms the observations, is the knowledge obtained that *all ions, which reduce when discharged, are again converted by this reduction performance into the ionic state and are not at all separated.*

#### *b. Excess Potential and the Reduction Action.*

Although the evolution of hydrogen by galvanic action at platinized platinum electrodes is a well-nigh reversible phenomenon, it proves irreversible at all other cathodes.

To convert, in a given electrolyte, a gram-equivalent of hydrogen from the ionic into the molecular state at atmospheric pressure, the same amount of work, which is, of course, dependent upon the beginning and end condition, is always required. But the electrical work is different at different electrodes and, since the same quantity of electricity is combined with a gram-equivalent of hydrogen, the potential of hydrogen evolution is different with the individual metals. Naturally, with the equality of the initial and final state the surplus of the electrical work performed must be compensated by an equivalent gain in work. Calorific phenomena probably accompany the increase in required work necessary for the hydrogen evolution; the results of experimental work on this subject, however, are not yet at our disposal. *Excess potential* is the excess of the discharge potential of hydrogen over the potential value of a

<sup>1</sup> D. R. P. 117007 (1900) of C. F. Boehringer u. Söhne; Löb and Moore, *Ztschr. f. phys. Chemie* 47, 418 (1904).

hydrogen electrode in the corresponding electrolyte. The quantity of heat produced by the excess potential can be very considerable. If we designate the absolute potential of the reversible hydrogen evolution by  $a$ , and the value of the excess potential by  $e$ , then the electrical work in the separation of a gram-equivalent of gaseous hydrogen in the first case is

$$A = 96540a;$$

and in the second

$$A_1 = 96540(a + e).$$

Since the total work in both cases must be equal, there results, as assumed, a production of a quantity of heat  $q$  occurs, the equation

$$96540a = 96540(a + e) - q,$$

$$q = 96540e.$$

For mercury  $e$  is = 0.78 volt, from which  $q = 18026$  cal. results.

$$[96540 \text{ coul.} \times 1 \text{ volt} = 23110 \text{ cal.}]$$

According to Caspari,<sup>1</sup> these excess potentials have the following values with individual metals:

At platinized platinum.....	0.005	volt.
“ bright platinum.....	0.09	“
“ nickel.....	0.21	“
“ copper.....	0.23	“
“ tin.....	0.53	“
“ lead.....	0.64	“
“ zinc.....	0.70	“
“ mercury.....	0.78	“

Ernst, who introduced the conception of excess potential into the science of electrochemistry, accepts as the cause of these phenomena the varying solubility of hydrogen in the metals.

<sup>1</sup>Ztschr. f. phys. Chem. 30, 89 (1899).

Since the energy of reduction depends chiefly upon the height of the cathode potential, the higher the excess potential is the stronger the former must be, so long as hydrogen is the reducing agent.

A great number of facts agree<sup>1</sup> with this conception. The assumptions regarding the electrical reduction mechanism, according to which the discharge of hydrogen ions must be distinctly distinguished from their molecular separation, lead to the same conclusions. The reaction velocity of molecular formation from the discharged hydrogen ions is lowered at metals with excess potential, so that the division between molecular formation and reduction of the polarizer turns in favor of the latter. This retardation of hydrogen evolution is shown in the higher potential, in the excess voltage. With a high excess voltage in the discharging space stronger concentrations of discharged reactive hydrogen ions can accumulate, so that the reduction of bodies reducible with difficulty, which does not occur at platinized platinum electrodes, succeeds at zinc or mercury cathodes.

Since in the fundamental views a separation of hydrogen in or upon the cathode does not enter into the question, the close connection of this separation with the solubility of hydrogen in the metals cannot be conceived. In this case it is more plausible to think of the reaction being catalytically influenced by the metal. Accordingly, the platinized platinum would be the metal which would most strongly accelerate the reaction



The higher the excess potential the smaller the catalytic acceleration of the reaction, and hence the stronger the concurrent reduction.

<sup>1</sup> S. Tafel, *Ztschr. f. phys. Chem.* **31**, 227 (1900); Loh, *Ztschr. f. Elektrochemie* **7**, 320, **333** (1900-1901); Cochin, *Ztschr. f. Elektrochemie* **9**, 642 (1903).

<sup>2</sup> E. Müller gives a similar explanation, but does not mention the catalytic action, which is here particularly emphasized. *Ztschr. f. anorg. Chem.* **26**, 1 (1901).

The idea of excess potential is useful in applying the process of separating a certain kind of ions at unattackable cathodes. For reduction it has up to the present only been proved for hydrogen; it is nevertheless possible that the separation potential of every ion changes with the nature of the electrode, since the opportunity for the reaction of discharged ions being catalytically influenced to form stable molecules is always present. E. Müller<sup>1</sup> and Coehn<sup>2</sup> have shown that the excess potential phenomenon also occurs in anodic processes.

The generally disseminated idea, however, that the *excess potential of hydrogen* also plays a part in the case of attackable cathodes is untenable. With metals which furnish reducing ions—and each cation is capable of reducing—hydrogen does not take part, or at least plays only a secondary rôle. The specific reducing actions of copper, zinc, tin, and lead cathodes are not to be explained by the excess potential of hydrogen. Since attackability is also a function of the electrolyte, the rule of excess voltage may be applicable in one case and not in another. For example, Tafel<sup>3</sup> could explain the strong reducing action of a lead cathode in sulphuric-acid solution by the high excess potential of the lead, while the same metal is attackable in alkaline electrolytes and yields reducing ions, whereby the hydrogen action seems excluded.<sup>4</sup>

### *c. Concerning Substances Reducible with Difficulty.*

Besides the discussion on the strong depolarizers thus far considered, it will be well to make a few special remarks on substances reducible with difficulty. The insight into the theoretical relations here existing has not yet been cleared up, and is much more difficult than in the case of the substances which consume practically all the cations which are discharged. However, it is not at all necessary to add special views to those already generally developed. They suffice for the present

<sup>1</sup> Jahrb. f. Elektrochemie VIII, 292; Ztschr. f. anorg. Chem. 26, 1 (1901)

<sup>2</sup> Ztschr. f. Elektrochemie 9, 642 (1903).

<sup>3</sup> Ztschr. f. phys. Chemie 34, 199 (1900).

<sup>4</sup> Cf. Löb and Moore, Ztschr. f. phys. Chem. 46, 427 (1904).

in explaining the phenomena occurring here, and we may possibly get along with a uniform interpretation. The deciding importance of reaction velocities on the course of every chemical action requires of us a clear explanation of the relation of the influences cooperating in the course of the reaction to that fundamental factor, the velocity of reaction. It will, therefore, be well to consider these influences from this particular side and to ask what relation do the electrical factors bear to the reaction velocity, and in what manner do they act on the latter. It appears that the reducing action of difficultly reducible substances at unattackable cathodes takes place differently, depending upon the material of the latter. This diversity can be explained by unequal reduction velocities. The latter depend upon the concentration of the reacting substances which so far as the ions alone to be taken into consideration are concerned is regulated by the current strength, the chemical resistance of the system, i.e. the nature of the medium, and by catalytic influences which, with the choice of suitable conditions, are to be ascribed to the electrode metal. The measurable electrical factor, the potential, comprises a part of these influences, and it is of consequence to thus know the single moments determining the potential in such a manner that the connection with the reaction velocity remains clear.

Substances reducible with difficulty are such possessing trifling polarizing value, and whose addition to the electrolyte unessentially lowers<sup>1</sup> the cathode potential which was determined for the pure electrolyte. The relations existing here have been fully investigated by Tafel and his pupils.

In the case of substances of this nature, reduced in acid solution at practically unattackable cathodes, the consumption of hydrogen by the depolarizer is never equal to the quantity of hydrogen liberated by the current, so that a division

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<sup>1</sup> With caffeine and succinimide, in sulphuric-acid solution, an increase in potential occurs at certain electrodes (see below) (Naumann: Concerning the Influence of the Cathode Potential on the Electrolytical Reduction of Substances Reducible with Difficulty) Thesis. Würzburg, 1904.



always takes place into hydrogen consumed by the reduction, and hydrogen evolved molecularly as a gas. According to the preceding explanations, it is clearly evident that the excess potential must play a decisive part in all these reactions; it forms an expression for the above-mentioned ratio of division in proportion to the reaction velocities. If we consider the velocity of formation of molecular hydrogen as a process influenced catalytically by the electrode material, the value of the excess potential of the electrode in pure acid without the depolarizer will be decisive for the reduction energy, provided that the catalytic property is not modified by the depolarizer. The latter, under similar experimental conditions, and provided no catalytic acceleration of the reduction itself occurs, reacts always with a similar velocity with the hydrogen. Thus a change in the division ratio between hydrogen evolution and reduction is only determined by a change in velocity of the former. Naumann's<sup>1</sup> experiments agree with this. He showed that the velocity with which caffeine is reduced at lead cathodes depends upon the cathode potential in pure acid. The reduction occurs the more energetically the higher the excess potential is in pure acid. This rule does not apply when the cathode metal materially influences the actual velocity of reduction, the reaction between hydrogen and the depolarizer. Thus caffeine is reduced more quickly at mercury than at lead electrodes, although both metals possess the same cathode potential, or the same excess potential in pure acid. The velocity of the molecular evolution of hydrogen can also be retarded by the presence of the caffeine molecules, as the caffeine molecules, to use a crude illustration, increase the chemical resistance in this reaction at the electrode surface. In this case the excess potential increases, and with it the cathode potential. At the same time the depolarizing action of the caffeine seeks to lower the cathode potential. If the first action—with small quantities of caffeine—is the stronger, an increase in potential is at first observed in spite of the addition of caffeine. By adding larger quantities

<sup>1</sup> See note on page 24.

of caffeine, the potential is finally caused to drop (by stronger depolarizing effects). This phenomenon occurs at lead but not at mercury cathodes (Naumann). In the latter case only the depolarizing action of caffeine is shown; this is perhaps dependent upon the different surface conditions of lead and mercury.

The cathode potential is determined on the one hand by the electrolytic osmotic pressure of the cathode, i.e., by the quantity of hydrogen which is evolved electrolytically at unattacked cathodes in the unit of time. With this hydrogen, the ions discharged in the boundary layer, which unite to form molecular hydrogen, are in equilibrium. This electrolytic osmotic pressure is, therefore, independent of the quantity of hydrogen used by the depolarizer. Moreover, the potential is determined by the concentration of the hydrogen ions in the electrolyte, which concentration can be taken as constant when strong acids are used.

The conclusions (likewise found by Naumann) to be drawn from these considerations<sup>1</sup> are the following: At mercury cathodes, whose excess potential is not influenced by the caffeine, the cathode potential must so adjust itself at every moment during the reduction as if only the electrolytic evolution of hydrogen occurred and the current consumed in the reduction of the caffeine did not influence its height. At lead electrodes, however, the cathode potentials are always somewhat higher during the reduction than in the same electrolytic hydrogen evolution in the pure acid, since the increase in excess potential caused by the caffeine is added to it.

It is evident—from a consideration of these variously possible influences, such as the change in the excess potential caused by the depolarizer, the catalytic action of the metal upon the velocity both of the molecular formation of hydrogen and the reaction between hydrogen and the depolarizer—that the value of the cathode potential is conditioned by a series of

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<sup>1</sup> Naumann, in his dissertation, gives another deduction which, however contains the hypothesis that the hydrogen formation and the reduction reactions are of the same order.

moments which can be independent of one another. Hence the reduction effect can vary even with equal potentials at different electrodes, which is true, for example, with caffeine at lead and mercury cathodes.<sup>1</sup>

### B. Anodic Processes.

A theoretical insight into this part of the electrolysis of organic compounds is much less clear than in the case of cathodic processes.

The pure action of oxygen is in every way comparable with that of hydrogen. Only a greater variety is here possible, because ozone as well as oxygen can be formed. At platinum electrodes, for instance, the formation of oxygen occurs at 1.08 volts as measured with a hydrogen electrode at zero value, and that of ozone at 1.67 volts. Moreover, the great susceptibility of the carbon compounds towards oxygen, as already alluded to, which may easily lead to their complete destruction, and the great number of oxidation phases to which each molecule may in a greater or less degree be subject, render difficult an insight into the electrical oxygen actions.

It has already been mentioned that the excess potential phenomenon occurs also with the oxidation phenomena. Thus it is possible to convert p-nitrotoluene into p-nitrobenzoic acid at lead-peroxide anodes, while at platinum anodes only the alcohol is formed. It still seems inexplicable how this peculiar action of the anode material takes place. The simplest yet sufficient explanation is to assume that the anode is capable of influencing catalytically the oxidation process as well as the formation of molecular oxygen. If the first process is accelerated and the second retarded, we obtain the excess potential by which the evolution of oxygen occurs only at a higher potential. Inversely, the oxygen and ozone formation can be made reversible, and the oxidizing action decreased.

A further complicating moment in electrolytic oxidations, as opposed to reductions, is the variety of possible ionic actions.

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<sup>1</sup> Tafel and Schmitz, *Ztschr. f. Elektrochemie* 8, 281 (1902).

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<sup>1</sup> Tafel and Schmitz, *Ztschr. f. Elektrochemie* 8, 281 (1902).

While the process at the cathode always ends finally in withdrawal of oxygen or in taking up of hydrogen, the number of possible reactions at the anode—aside from solution-phenomena, which are without interest here—is a much greater one. For, each ion which is capable of substituting can pass into the reactive state at the anode and produce reactions which cannot be numbered with the real oxidations. In the first place numerous substitutions can occur in difficultly oxidizable bodies, especially aromatic compounds, for instance the chlorination of phenols and phthaleins, nitration of acids, diazotizing of amines, etc. Substitution and oxidation processes often occur simultaneously, as in the electrolytic formation of iodoform from alcohol.

A great many more individual varieties of reactions must be taken into consideration in anodic processes. However, the same fundamental law holds good for each of the separate possible processes as with the reductions, in that the energy of the action of the anion is determined by the anode potential.

Thus O. Dony Hénault,<sup>1</sup> carefully observing limited anode potentials in the electrical oxidation of the alcohol, could obtain acetaldehyde or acetic acid at will.

The reason for the prominence of reduction processes as apposed to the less prominent electrical oxidations has already been given. Besides the complexity of the phenomena, it must be taken into consideration that the oxygen evolved at platinum anodes has a low potential. The action of an oxidizer depends upon the oxidation potential with which the oxygen attacks the depolarizer. Even though the oxidation potential can, within certain limits, be varied by the anode potential, for instance by the material of the anode, it nevertheless does not attain the value of the strong chemical oxidizers, as for example chromic acid or permanganic acid. This follows from the small activity of electrolytic oxygen in regard to separate bodies.

Since it is not possible always to obtain the entirely indi-

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<sup>1</sup> Ztschr. f. Elektrochemie 6, 533 (1900).

vidual action of these two bodies on organic compounds with the aid of electrolytically evolved oxygen, it seemed advisable to use the chemical oxidizers, which have already been mentioned, in the electrolytic cell. This was done by employing the electrical process only for the regeneration of the chromic or permanganic acids which, as such, oxidize organic bodies in a purely chemical way, being themselves converted thereby into lower stages of oxidation. The advantage of such a method lies in a saving of both the oxidizing acids, because, on account of the regeneration to their highest state of oxidation, very small quantities suffice to oxidize unlimited quantities of organic bodies. This oxidation process is hence both a secondary and a chemical one. Nevertheless, it possesses the essential features of an electrochemical process, the substance being replaced by the energy.

Attackable anodes, which are brought into solution by the anions of the electrolyte, are of no value, or only of a wholly secondary one, in the electrolysis of organic compounds. But in such cases where, by reason of the attackability, oxidizing substances are formed on the anode, the latter can assume the functions of an oxygen carrier. Thus, if a lead anode is superficially coated with lead peroxide, this latter effects the oxidation, being in turn reduced but always regenerated by the current. But if a lead-peroxide anode, prepared in this manner, acts merely by means of its excess potential for the discharged oxygen, without reacting directly with the depolarizer, it naturally exercises only the functions of an unattackable anode.

Finally may be mentioned the purely catalytic action of the electrodes upon the reaction products produced by the electrolysis, a sphere of phenomena which lies outside the purely electrical relations. This is the case, for instance, in the decomposition of hydrogen peroxide by electrical oxidation at platinum anodes into water and oxygen. But even the electrical conditions can be modified by such reactions, if changes in the concentration relations of the predominating ions are combined with them.

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## 7. THEORY OF THE REACTION VELOCITY IN ELECTROLYTIC PROCESSES.

The ease with which the reaction conditions can be controlled makes electrolytic processes especially adapted for studying the laws of reaction, particularly those of reaction velocities. The dependence of the reacting agents upon the current strength, according to Faraday's laws, makes it possible to vary *ad libitum* the temporal total course of a reaction within wide limits—a possibility which in purely chemical operations, by changing the conditions of pressure and temperature, exists to a far less extent.

Attempts have not been lacking to regard electrical processes from a reaction-kinetic point of view, and to use them directly for determining reaction velocities. Even though these experiments are based naturally upon single simple examples—mostly reduction experiments—their theoretical results have, especially for physicochemical speculations of organic reactions, such general importance that the reasoning involved in the most important theories will briefly be outlined here.

*a. The Diffusion Theory.*

Since, according to the preceding descriptions, the reaction space of electrolytic processes consists of an extremely thin layer in contact with the electrode—the contact surface of electrolyte and electrode—these processes can generally be regarded as reactions in heterogeneous systems. Nernst<sup>1</sup> has proposed a theory for such systems, which has been tested experimentally by Brunner.<sup>2</sup> The principle of this theory consists in basing the reaction velocities on the diffusion velocity.

The equilibrium between two phases at their boundary surface must be produced with extremely great rapidity,

<sup>1</sup> *Ztschr. f. phys. Chemie* **47**, 52 (1904). See also the earlier investigation: Noyes and Whitney, *ibid.* **23**, 689 (1897)

<sup>2</sup> *Ztschr. f. phys. Chem.* **47**, 53 (1904)

otherwise infinitely great, or at least very great, forces would develop between the extremely close points between which the reaction occurs. These would, however, bring about the equilibrium practically instantly. In such a case the reaction velocity is conditioned by the velocity with which the mobile components reach the border-line of the phases, i.e. by the diffusion velocity.

The contact surface of both phases will now actually possess a thin but measurable layer of the thickness  $\delta$ , within which the whole diffusion process occurs.

If we designate the concentration of the diffusing substance at the surface of the fixed phase by  $C$ , its concentration in the solution by  $c$ , its diffusion constant by  $D$ , and the surface of the solid body by  $F$ , then in the period  $dt$  the quantity of substance

$$dx = DF \frac{C - c}{\delta} dt$$

will diffuse to the contact surface and immediately react. The speed of reaction becomes

$$\frac{dx}{dt} = DF \frac{C - c}{\delta}.$$

If we consider that  $C$  possesses an extremely small and negligible value, on account of the equilibrium which occurs instantly, the following equation results:

$$\frac{dx}{dt} = \frac{DF}{\delta} \cdot c.$$

The speed of reaction is proportional to the concentration of the diffusing substance.

In applying these results to electrochemical reactions there is to be added only the condition that the concentration of the reacting substance in the immediate vicinity of the electrode must always possess a very small value, which can easily be attained by choosing a suitable current tension. Then the reaction velocity will depend only upon the quantity of



the substance reaching the electrode. Electrolytic transference must be considered as well as the diffusion, if ions are involved.

Since the quantity of the discharged ions depends upon the current strength, it represents a measure of the reaction velocity, if (1) side reactions are excluded—for instance, if no ions are discharged without reacting—and (2) the current strength chosen is not so small that the reaction velocity possesses a higher value than the discharging velocity of the ions regulated by the intensity.

In other words: The current strength is then only a direct measure of the reaction velocity, if the maximum current strength at which all the liberated ions are just able to react is employed. The production of this condition can be easily recognized experimentally by the fact that the least increase of this maximum intensity leads to side reactions, most frequently to a molecular separation of the discharged ions.

Before the Nernst theory was proposed, H. Goldschmidt<sup>1</sup> had already employed this idea for studying the relation between reaction velocity and concentration of aromatic nitro-bodies.

If the maximum current strength at which no hydrogen is yet evolved is designated by  $J_m$ , the concentration of the body to be reduced by  $C$ , the experimental equation resulted

$$J_m = K \cdot C^{\frac{1}{2}}.$$

$C^{\frac{1}{2}}$  is the concentration of a cross-section, i.e. the reaction takes place directly at the electrode surface. If we suppose that the adjustment of the equilibrium takes place there with extreme rapidity, according to Nernst, then the reaction velocity will have to be based solely on the diffusion velocity, and will, therefore, be directly proportional to the concentration of the depolarizer in the electrolyte. The theory hence demands the formula

$$J_m = K \cdot C.$$

<sup>1</sup> Ztschr. f. Elektrochemie, 7, 263 (1900).

The lack of conformity has not yet been explained. Perhaps the supposition of a very rapid attainment of the equilibrium at the electrode does not apply to the reduction of nitrobenzene, which abounds in phases.

The results of Åkerberg<sup>1</sup> concerning the velocity of the electrolytic decomposition of oxalic acid in the presence of sulphuric acid agree better with the theoretic requirements. So long as the proportion of oxalic acid is considerable, the decomposition takes place according to Faraday's laws, i.e. without evolution of oxygen. But if the solution has reached a certain dilution, the electrolysis occurs—independently of the current density—accompanied by an evolution of oxygen proportional to the concentration of the oxalic acid in the solution. The decomposition of the oxalic acid then takes place in the same proportion as new oxalic acid diffuses from the electrolyte to the electrode boundary surface. Consequently, according to Nernst's theory, the electrolytic oxidation velocity henceforth becomes a diffusion velocity.

The hypothesis of the latter is always the instantaneous equilibrium at the contact surface of heterogeneous phases; but the fulfillment of this condition is not to be accepted forthwith, particularly in the case of many organic processes which—for instance, the reduction of nitro-bodies—are able to give a whole series of intermediate phases up to the final equilibrium.

The influence of the electrode material upon the velocity of reaction decides particularly against its significance in all cases as a diffusion velocity.

Finally, to view electrolytic processes as heterogeneous systems does not seem at all sound, according to the description of the electrochemical reaction mechanism given in our introduction. If the first process, in accordance with the given exposition, is the discharge in the electrode boundary surface, and if the second is the separation on the electrode or the

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<sup>1</sup> *Ztschr. f. anorg. Chemie* **31**, 161 (1902). See also Brunner, *Reaction Velocities in Heterogeneous Systems*, p. 52. Thesis, Göttingen, 1903. Cf. also Luther and Brislee, *Ztschr. f. phys. Chemie* **45**, 216 (1903).

reaction of the ions present in the boundary surface with the depolarizer, hence in the fluid system, then the actual reaction takes place in a homogeneous system. The typical influence of the reacting ions will then show itself in the velocity constant of this reaction; likewise, if the ions are derived from the latter, the typical effect of the electrode metal will be seen. A sharp distinction will then exist between the discharge, which can occur with an extremely great velocity, and the actual chemical reaction with the depolarizer, the velocity of which will be measurable and distinctly individualistic. In this case the velocity of diffusion alone cannot represent the velocity of reaction.

With the aid of other ideas concerning the electrical reaction mechanism, particularly the reduction mechanism, Haber and Russ<sup>1</sup> arrive at the same interpretation. They advance the proposition: "The reducing phase is formed at the cathode with an immeasurably great velocity constant, but the velocity with which it acts chemically on the depolarizer depends upon the latter's peculiarities and is often measurably small."

By a "reducing phase" is meant hydrogen or any metal phase which is supposed to stand in a dynamic equilibrium with it, so that the action of the different cathode materials can be taken as equal, a condition which can be experimentally obtained by the choice of a cathode potential which remains always the same.

#### *b. Osmotic Theory of Electrical Reduction.*

Haber<sup>2</sup> was the first to publish a theory of electrical reduction which is in many points free from the limiting conditions of the diffusion theory. Later, conjointly with Russ,<sup>3</sup> he brought it to the form given below.

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<sup>1</sup> Ztschr. f. phys. Chemie **47**, 263 (1904).

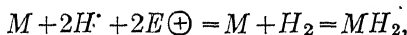
<sup>2</sup> Ibid. **32**, 193 (1900).

<sup>3</sup> Ibid. **47**, 263 (1904).

The sphere of validity of this theory, in conformity with the experimental material, extends to the use of unattackable cathodes at current strengths which, in contradistinction to those chosen by Goldschmidt, lie considerably below those necessary for developing hydrogen. The conditions are hereby simplified, because, on the one hand, the reduction must proceed exactly according to Faraday's laws, and, on the other hand, it can be regarded as being always accomplished by the same agent, hydrogen. This latter hypothesis, since it permits the assumption that the reducing agent obeys the laws of gases, is extremely weighty for the theory. Herewith is assumed that the hydrogen is present in the electrode surface with the concentration  $C_H$ . If we want to assume the replacement of the hydrogen by a metal, the latter must also be regarded as obeying the laws of gases. It hence suffices to deduce the theory only for hydrogen as a reducing agent. If  $C_H$  be the concentration of the hydrogen atoms at the cathode, then the potential  $E$ , according to Nernst's osmotic formula, is

$$E = RT \ln \frac{C_H}{C_H'},$$

in which  $R$  is the gas constant, and  $T$  the absolute temperature. If the hydrogen in the cathode now reacts with the depolarizer  $M$ , for instance according to the equation



the speed of reduction is

$$-\frac{dC_M}{dt} = kC_{H'}^2 \cdot C_M - k' C_{MH_2},$$

or, neglecting the subtractive member,

$$-\frac{dC_M}{dt} = kC_{H'}^2 \cdot C_M.$$

According to the above-mentioned hypotheses, we can directly substitute the current strength  $J$  for the speed, which

is proportional to it,

$$-\frac{dC_M}{dt} = k_1 J,$$

$$\frac{k_1 J}{k C_M} = C_H^2 \quad \text{or, more simply,} \quad \frac{J}{k'' C_M} = C_H^2,$$

$$C_H = \sqrt{\frac{J}{k'' \cdot C_M}}.$$

If this value is introduced into the potential equation,

$$E = RT \ln \frac{C_H}{C_H'},$$

there results

$$E = \frac{RT}{2} \ln \frac{J}{k'' C_M \cdot C_H'},$$

or if  $C_H'$  is considered as constant, and the constant  $k'$  is placed in the formula as subtractive member,

$$E = \frac{RT}{2} \ln \frac{J}{C_M} - \text{const.}$$

The relations were now tested for the constant  $J$  in an alcoholic nitrobenzene solution; as a result the formula can also be written in the following manner:

$$E = \frac{RT}{2} \ln \frac{1}{C_{\text{C}_6\text{H}_5\text{NO}_2}} - \text{const.};$$

furthermore, for constant nitrobenzene concentration,

$$E = \frac{RT}{2} \ln J - \text{const.},$$

and finally for constant cathode potential, the relation

$$\frac{J}{C_{\text{C}_6\text{H}_5\text{NO}_2}} = \text{const.}$$

So far as a logarithmic connection between  $E$  on the one hand, and  $J$  and  $C_M$  on the other resulted, the theory is veri-

fied by the observation. However, the constant factor before the logarithm was not found at  $\frac{RT}{2}$ . It always possessed a larger and somewhat variable value.

Haber and Russ<sup>1</sup> therefore changed the original formula to

$$E = x \left( \frac{RT}{2} \ln \frac{J}{C_M} - \text{const.} \right).$$

This expression was substantiated by experience when the influences of diffusion were avoided as much as possible. The factor  $x$  appears as a function of the electrode condition

It would lead too far to enlarge upon the meanings of the factor  $x$  which were discussed by Haber and Russ.<sup>2</sup>

### *c. Summary of the Theories.*

The two theories of Nernst and Haber above mentioned seem to contradict one another in important points. The electrical speed of reaction in the diffusion theory (Nernst) is directly a speed of diffusion; Haber's formula holds good only in case the diffusion is excluded as much as possible.

The contradiction is only an apparent one, and the difference between the theories lies in the hypotheses. The measurement of the speeds of reaction depends upon the conditions of the experiment. If the reaction between two components of reaction actually takes place instantaneously, we can vary the time of reaction entirely at will by the period of time during which we add *one* of the components. If the latter is used up with immeasurable rapidity, the measured velocity of reaction must naturally always remain proportional to the added quantity of the reaction components. The Nernst theory is based on relations in which this subsequent delivery is effected only by the diffusion, the reacting agent furnished by the current being

<sup>1</sup> Ztschr f phys Chemie 47, 264 (1904).

<sup>2</sup> Cf. also: Russ, Concerning Reaction Accelerations and Reaction Retardations in Electric Reductions and Oxidations. Ztschr. f. phys. Chemie 44, 641 (1903) See also the chapter on electrode material.

kept at the electrode by the potential relations in an infinitesimal concentration as opposed to the external concentration. Since the reaction can only proceed further if new quantities of the agent reach the electrode, and this subsequent delivery can be brought about only by transference and diffusion, the first conclusion drawn is that these two factors determine the current strength. The current can reach the electrode only by means of ions. Since, moreover, the measurable velocity of reaction is regulated by the current strength, it follows further that this velocity of reaction is also regulated by the effects of diffusion and transference. It is mentioned in Åkerberg's experiments what the ratios are in the presence of a depolarizer. The theory holds good if the measurable speed of reaction, which need not be identical with the actual velocity, is artificially made a diffusion velocity. The considerations of Haber suppose that the ions and depolarizer are in such great concentrations at the electrode that the ions derived from the great surplus bring about the reaction in accordance with the current strength—*independently* of that which is subsequently delivered by diffusion. The relations of Haber are therefore valid only in such cases where impoverished phenomena are excluded at the cathode. Those of Nernst are true only in such where complete impoverishment exists, i.e., where almost zero concentration of the depolarizer is created at the direct border line of reaction. For the reaction can progress only in this case in the same proportion as the depolarizer enters by diffusion into the reaction layer.

We easily obtain results having the advantage of better proof, if we base the reaction-kinetic speculations upon the views developed on the reaction mechanism, according to which the discharge of the ions at the electrode is strictly to be distinguished from the separation on the electrode or the reaction with the depolarizer. This kind of proof is naturally of greater significance for the Haber than for the Nernst deductions. For even if the whole reaction, according to our supposition, takes place in the fluid phase, i.e. in a homogeneous system, the principles of the reaction can practically be appli-

cable in heterogeneous systems. In the localization of the discharging space in the immediate vicinity of the electrode, the layer in which the discharged ions are present may be considered as an extremely thin film which behaves as a heterogeneous formation towards the electrolyte. The concentration of the discharged ions in this film is undoubtedly extremely small at the great velocity of reaction with which they separate or react. Thus the progress of the reaction depends upon the velocity with which diffusion and transference conduct new ions to this film. If the concentration of the depolarizer is strong, only the last-mentioned factors will influence the reaction velocity; if it is weak, the quantity of the depolarizer, which is supplied by diffusion, plays an important part.

Our views, that the laws of gases can actually be applied to the concentration of the discharged ions, form a desirable confirmation of Haber's relations. For the discharged ions, which are not in or upon the electrode but in the solution, must have an osmotic pressure proportional to the concentration in the discharging space, i.e. the current strength, according to Haber's conditions. The validity of the laws of gases, if we suppose a solid solution of the ions in the electrode, is difficult to explain, particularly if the case is one of metal ions which reach the cathode and there produce reduction effects. The deductions of Haber remain unchanged formally, but their sphere of validity appears enlarged, however, since under the necessarily limited conditions the behavior of attackable cathodes becomes also theoretically representable. A repetition of these deductions, however, will not be given here.

The theoretical treatment of the physicochemical material, which organic chemistry places so abundantly at our command, is yet in its initial state. Not only do the many obscure points incite to a continuation of the work, but the few results and the numerous problems rather justify the opinion that the phenomena of organic electrolysis are especially adapted to carry the teachings of physical chemistry into the domain of organic chemistry.



## CHAPTER II.

### METHODICS.

It is assumed that the reader is familiar with the general arrangements of electrochemical experiments. In the following pages only those particulars will receive attention which are of special importance in the electrolysis of organic compounds. The arrangement which permits the observation of the decisive potentials, and their control and maintenance at a constant, is particularly important. Of importance are certain electrolyzing apparatus suitable for particular purposes, and also arrangements for stirring, which often decisively influence the course of an experiment.

#### 1. THE CELLS.

Cells of the most varied constructions, depending upon the problem in hand, are required. The conductivity of the electrolyte, the necessity of collecting gases, the separation of the cathode and anode chambers, regulation of the temperature, the variation of the size of the electrode, all demand certain requirements and arrangements.

Of course, the comprehensiveness of the experiment is also of great importance. However, only the conditions which enter into the question of scientific investigations are of interest here. We shall, therefore, waive the repetition of the technical arrangements for organic electrochemical processes.

In the simplest case it suffices to immerse the two electrodes always in a certain position in a glass vessel, and usually parallel to one another. The vessel is closed with a hermetically fitting stopper when gases are to be collected. Three

be obtained by putting in glass or porcelain worms through which a continuous current of water is conducted. Metallic worms must only be used if they are to serve at the same time as electrodes. Otherwise they act in an undesirable manner as intermediate conductors in the electrolysis. Often it is impor-

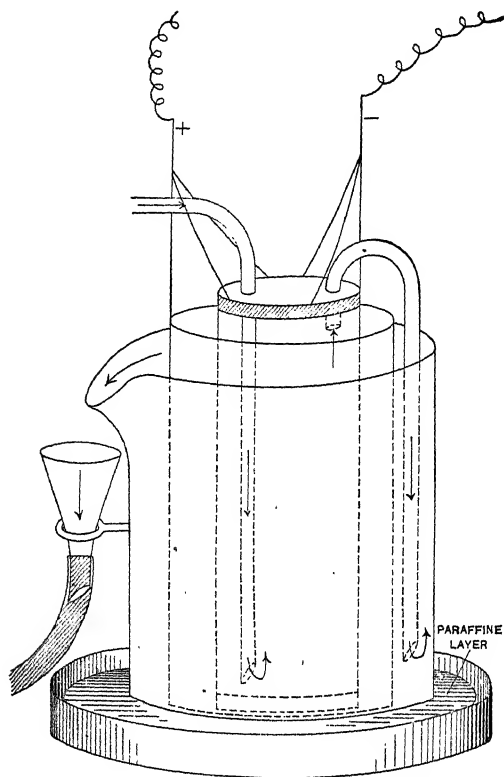


Fig. 1.—Arrangement for Cooling the Electrodes.

tant to keep the electrodes cool, since their surfaces limit the actual reaction space.

Cooling of the electrodes is done either by using worm electrodes, as above mentioned, or, if this is made impossible by the nature and form of the electrodes, by choosing hollow, cylindrical electrodes,—through which water is passed,—and of

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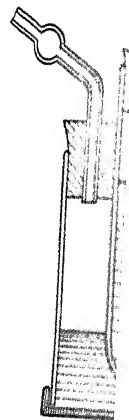


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<sup>1</sup> Ztschr. f.

<sup>2</sup> Ber. d. de

<sup>3</sup> Lobb, Ztsch

perforations are required in the stopper, one for a glass tube, and the other two for the electrodes, the latter being sealed in. A little mercury closes the circuit. Changes in temperature are obtained by outwardly heating or cooling the vessel. Stirring is caused by the electrolytically evolved gases.

The current conditions can be varied in the most different ways. By a choice of concentrations, or by additions, the conductivity can be increased or diminished; also by raising or lowering the voltage. The height of the electromotive force developed in the cell determines the current strength; the ratio of the latter to the electrode surfaces gives the current density, and to the volume of the electrolytes, the current concentrations.<sup>1</sup>

This simplest form of arrangement seldom suffices; usually a separation of the cathode and anode spaces is required. This is oftenest obtained by the use of a diaphragm, or by connecting, with a siphon arrangement, two separate vessels,—one containing the anode and the other the cathode fluid; this latter method is more rarely used, however, because the resistance is liable to become too great. Porous earthenware cylinders or plates are usually employed as diaphragms. Diaphragms, which often answer well, are sometimes made of gypsum, pressed asbestos (only utilisable in alkalis<sup>2</sup>), porous cement, and parchment paper. So-called "acid-proof" diaphragms are also used. Cylindrical vessels are simply placed in the wider outer vessel, and plates are fitted in tightly, or cemented in. A simpler method is to make the cell of two separate parts fitting upon one another. Between these the diaphragm plate is tightly wedged with screws by means of a rubber ring or a caoutchouc frame. The Wehrlin<sup>3</sup> cell is made in this fashion. Cooling and stirring in electrolytical experiments are of special importance. Aside from the external cooling of the electrolyte, a constant temperature of the latter can

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<sup>1</sup> Tafel, *Ztschr. f. phys. Chem.* **34**, 201 (1900).

<sup>2</sup> LeBlanc, *Ztschr. f. Elektrochemie* **7**, 290 (1901).

<sup>3</sup> *Ibid.* **3**, 450 (1897).

be obtained by putting in glass or porcelain worms through which a continuous current of water is conducted. Metallic worms must only be used if they are to serve at the same time as electrodes. Otherwise they act in an undesirable manner as intermediate conductors in the electrolysis. Often it is impor-

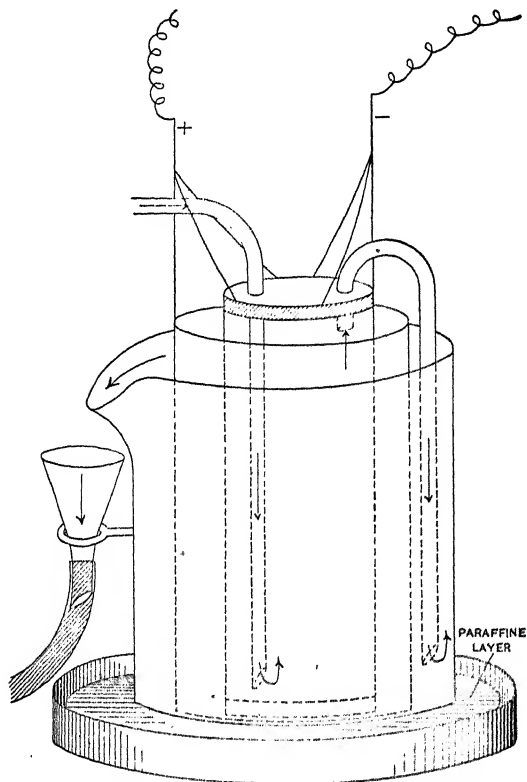


FIG. 1.—Arrangement for Cooling the Electrodes.

tant to keep the electrodes cool, since their surfaces limit the actual reaction space.

Cooling of the electrodes is done either by using worm electrodes, as above mentioned, or, if this is made impossible by the nature and form of the electrodes, by choosing hollow, cylindrical electrodes,—through which water is passed,—and of

the shape first proposed by Löb<sup>1</sup> and later modified by Tafel.<sup>2</sup> Figs. 1-4 represent types of electrolytic cells variously employed.

It is evident from the drawings that, by choosing suitable diaphragms, the reaction chambers can be closed from without.

In using earthenware cylinders, the reaction fluid—anodic or cathodic—is most suitably placed in the earthenware cylinder, especially if the gases are to be determined.

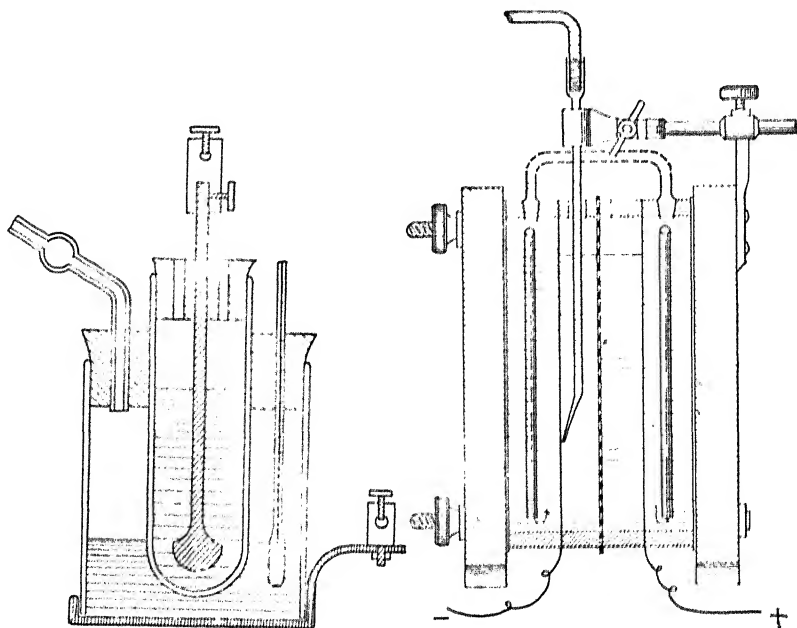


FIG. 2.—Tafel's Electrolytic Cell.

FIG. 3.—Wehrlin's Cell.

Gas or mechanical stirrers are made use of for stirring the electrolyte. Mechanical stirrers, however, are employed only if the electrolytic gases are to be investigated, unless these suffice for the stirring, as is the case in experiments with high current strengths. By permitting the base of the stirrer to dip into mercury,<sup>3</sup> the mechanical stirring can easily be arranged in a manner so as to obtain a hermetical seal.

<sup>1</sup> Ztschr. f. Elektrochemie 2, 665 (1896).

<sup>2</sup> Ber. d. deutsch. chem. Gesellsch. 33, 2223 (1900).

<sup>3</sup> Löb, Ztschr. f. Elektrochemie 7, 117 (1900); Ztschr. f. phys. Chemie 34, 647 (1900).

The gas-tight electrode stirrers are based on the same principle. They have the advantage of using the electrodes themselves,—which may have any shape,—for stirring. A fine division of the components is thus assured on the electrode surface the (reaction space). This matter is of great importance in a series of reactions, for instance in the simultane-

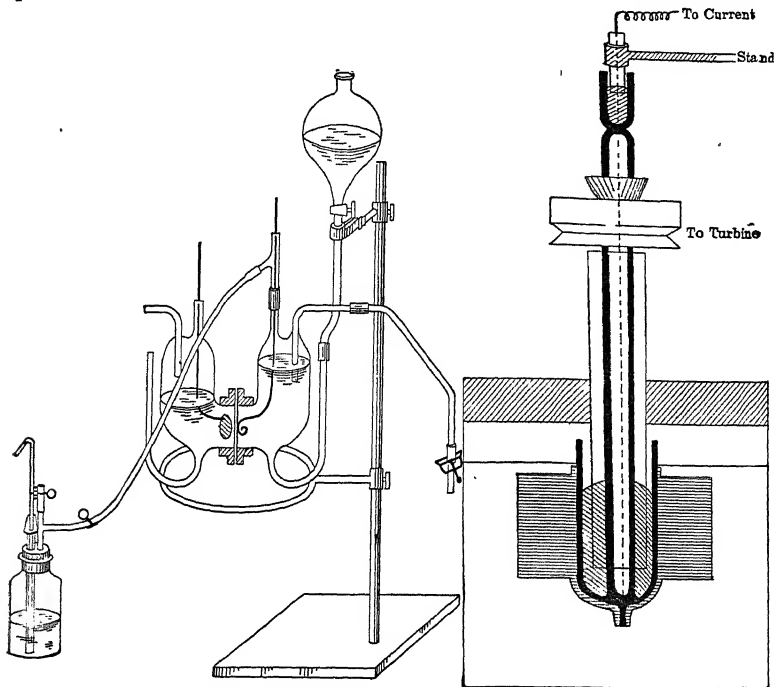


FIG. 4.—Electrolytic Cell (Hofer's)

FIG. 5.—Gas-tight Electrode Stirrer.

ous reduction of two nitro-bodies to a mixed azo-body, or in the electrolytic preparation of azo-dyes, etc. (See Fig. 5.)

The current is conducted through mercury, which is poured into the glass tube in which the electrode is sealed.

## 2. ARRANGEMENT OF EXPERIMENTS AND MEASUREMENTS OF POTENTIAL.

The typical arrangement for an electrical decomposition is that in which the main current flows through an ammeter and the

cell, and the terminals of a voltmeter, in branch circuit, are connected directly to two points at the electrodes.

The potential of the electrode at which the respective reaction takes place is of decisive importance on the course of the electrolysis; it may be the cathode or anode potential or sometimes both. The potential *difference* between the electrodes, which is influenced by many contingencies, such as the resistance of the diaphragm, etc., is, on the contrary, generally without importance for the reaction. The voltmeter shows the consumption of electrical energy only in combination with the ammeter.

The potential of an electrode is determined in combination with a second constant electrode which does not belong to the actual electrolytic system. This subsidiary or standard electrode, whose potential is either arbitrarily taken as zero or has a certain absolute value, is connected by a siphon with the liquid surrounding the experimental electrode. The electromotive force of this galvanic combination is then measured by one of the well-known methods, with a galvanometer or capillary electrometer. If the potential difference of the standard electrode is correctly subtracted from the obtained value, the difference in potential of the reaction electrode, based on the agreed-upon zero value of the potential, is obtained.

Two subsidiary or standard electrodes are in use, the calomel electrode of Oswald<sup>1</sup> and the hydrogen electrode of Nernst.<sup>2</sup> The former, consisting of a combination of mercury covered with mercurous chloride as depolarizer and immersed in a solution of  $\frac{1}{10}$  n-potassium-chloride solution, has, according to the best measurements, an absolute potential of 0.613 volt  $\pm$  0.0008 ( $t^\circ$  -- 18), in the sense that mercury is positive, the solution negative. The standard hydrogen electrode

<sup>1</sup> Ostwald-Luther, Physicochemical Measurements, p. 383, Leipzig, 1902.

<sup>2</sup> Ztschr. f. Elektrochemie 4, 377 (1898); 7, 253 (1900); see also Wilsmore, Ztschr. f. phys. Chem. 35, 291 (1900); Ostwald-Wilsmore, Ztschr. f. phys. Chem. 36, 91 (1901).

consists of a platinum sheet charged with hydrogen in a normal electrolyte, i.e. normal as to the hydrogen ions. In preparing the hydrogen electrode, the sheet platinum (or palladium) is arranged so as to lie half in the electrolyte and half in hydrogen gas, and the saturated state is maintained by having a constant current of hydrogen pass through the electrolyte. The half of the electrode not in the electrolyte must thus be surrounded during the entire time of the experiment by an atmosphere of hydrogen. Nernst gives the hydrogen electrode the arbitrary value 0.

Depending upon the form of the cell, the connection with the standard cell can be made by means of a siphon or other method. Of course the electrolyte of the normal electrode must not react appreciably with that of the experimental cell, and in most cases it will be of value to separate both by a suitably adjusted diaphragm.

The problems to which the measurement of the electrode potential gives rise are manifold.

The task is often to determine at what potential a reaction begins; in other words, what discharge potential the separated or reacting ion possesses in the presence of the depolarizer. The determination of this value is most simply made by measuring the decomposition potential.<sup>1</sup> This method is based upon the fact that a permanent decomposition of an electrolyte can only take place by using a certain electromotive force which is just able to overcome that of the polarization. If we begin to polarize with a small electromotive force, the current cannot at first permanently pass the cell. Only when the electromotive force exceeds the value of the polarization does the sudden deflection—the “rebound” of a galvanometer enclosed in the circuit for observation—show the passage of the current, revealing the decomposition value of the electrolyte. If in a coordinate system the electromotive forces are considered as abscissas, the current strengths or deflection factors of the galvanometer as ordinates, then curves are obtained which show

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<sup>1</sup> Le Blanc, *Ztschr. f. phys. Chem.* 8, 299 (1891); 12, 333 (1893).



characteristic breaks at the decomposition values. If the electrode at which the reaction is expected to occur is combined with a normal electrode, and the difference in potential at the work-electrode is observed for increasing current strengths, it will be found that at a certain value of the latter, a sudden passage of the current, which appears as a break in the curve, occurs. This break is characteristic for the beginning of any kind of reaction, whether it be that of the separation of ions or their reaction with the depolarizer. When several kinds of ions are separated or react at different electromotive forces,<sup>1</sup> these breaks can repeat themselves in the curve.

The simplest method of determining the beginning or non-occurrence of a reaction consists in measuring the discharge potential of the cations or anions before and after the addition of the depolarizer which is to be acted upon. A change in potential at the addition shows the beginning of the reaction.

It is of especial importance to know the potential interval within which one or several distinct reactions take place. The determination of this depends upon the change in potential which the presence of a depolarizer produces as opposed to an electrolyte containing no depolarizer. For example, if it is desired to learn if chlorine derivatives of phenol can be prepared at the anode by electrolysis of a hydrochloric-acid solution of phenol, then the point of decomposition of the chlorine ion, in combination with the hydrogen electrode, is found at 1.31 volts in a  $1/1$  n-hydrochloric-acid solution. If phenol is added to this solution, the break in the curve occurs already at 0.9 volt.<sup>2</sup> Therefore the span in potential, within which the reaction for the formation of chlorine derivatives of phenol must take place, lies between 0.9 and 1.3 volts. In this manner Dony-Hénault, among others, determined the decomposition potential of the OH ions, in combination with the hydrogen electrode, in dilute sulphuric-acid solution both without and with the addition of ethyl alcohol. He found

<sup>1</sup> S. Glaser, *Ztschr. f. Elektrochemie* 4, 355, 373, 397 (1897); Bose, *ibid.* 5, 153 (1898).

<sup>2</sup> Cf. Dony-Hénault, *Ztschr. f. Elektrochemie* 6, 533 (1900).



is accomplished by setting the cell, which consists of the work-electrode and the normal electrode, at the desired tension by choosing the suitable polarizing current strength—according to the compensation method,—and by taking care that the tension existing between the work electrode and the standard electrode retains the value of the compensating potential by varying the current strength as may become necessary during the course of the experiment. Haber<sup>1</sup> has used this method of procedure for limited potentials, and Löb and Moore<sup>2</sup> employed it for an entirely distinct constant potential during prolonged electrolyses. Figs. 6 and 7 are sketches of the arrangements of their experiments. The requirements for the reduction of nitrobenzene, as expressed in the theoretical part of this book, were proved by these experiments,—namely, that, by reason of the necessary limitations, only the cathode potential is decisive for the obtainable reduction phase.

If in simpler cases, which are naturally rarer in organic electrolysis, the only point is to keep the total decomposition tension between the electrodes below a certain value, then it will suffice to employ suitably small electromotive forces, or such limited by branching.

Finally, the measurement of single electrode potentials is of importance in itself for obtaining the depolarizing values, i.e., the potential differences of an electrolyte in connection with a certain electrode with or without a depolarizer. It is evident that these depolarizer values are characteristic quantities for the chemical nature of the depolarizer, and are very closely related to the constitution and configuration of the molecule. Introductory experiments on this question for nitro- and nitrosobodies have been made by Panchaud de Bottens.<sup>3</sup> Löb and Moore<sup>4</sup> have also measured the depolarizing values for nitrobenzene at different electrodes and current strengths. It was

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<sup>1</sup> Ztschr. f. Elektrochemie 4, 507 (1898).

<sup>2</sup> Ztschr. f. physik. Chem. 47, 432 (1904).

Ztschr. f. Elektrochemie 8, 305, 332 (1902).

<sup>4</sup> Ber. d. 5. Internat. Kongr. f. angew. Chemie, Berlin, 1903, 4, 666.

found that they generally became smaller with increasing current strengths. Single electrode metals, however, show peculiarities which suggest the occurrence of variable reactions.

Besides the usual method of arrangement mentioned at the beginning of this chapter, in which the current derived from any suitable source of electricity passes through the cell, the apparatus can often be suitably simplified—especially for electrical reductions—by employing Löb reaction cells<sup>1</sup>

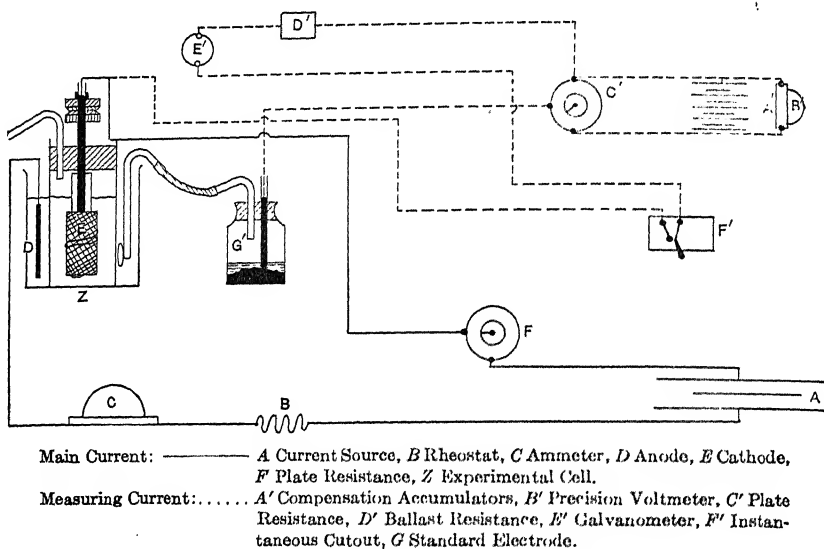


FIG. 7.—Löb's Experimental Arrangement.

or short-circuiting cells. Cells can be constructed, which do away with the primary-current production in laboratory work, based upon the fact, already used by Royer<sup>2</sup> in the reduction of oxalic acid, that a reaction producible by the current can inversely serve as a part of a suitably constructed electric cell. If, for instance, nitrobenzene is dissolved in concentrated sulphuric acid, the solution poured into an earthen ware cylinder, a piece of platinum dipped in the latter and the

<sup>1</sup> Ber. d. deutsch. chem. Gesellsch. 29, 1390 (1896).

<sup>2</sup> Compt. rend. 69, 1374 (1869); see also Lapeyrière, Tommasi, *Traité d'Electrochimie* 724, 729 (1899).

cylinder with its contents placed in another vessel containing dilute sulphuric acid in which is immersed a piece of amalgamated zinc, we have an electric cell or battery. On making a metallic contact between the zinc and platinum with a binding-screw, quite a considerable current circulates even at a low tension, since the resistance is small. After a few hours the contents of the earthenware cylinder solidifies, forming a pasty mass of amidophenol sulphate. Such systems can be prepared in very many suitable forms, particularly in such a manner that heat, or pressure, etc., can be applied during the operation.

### 3. THE ELECTRODES.

The nature of the electrodes is of great importance for the course of electrolytic processes. The material is not only decisive for the effect, as already fully discussed, but the nature of the surface and the previous treatment of the electrodes can decidedly influence the course of the electrolysis. In the first place it is obvious that the size of the surface wetted by the electrolyte is codeterminative for the potential and current density, and even on this account its smoothness or roughness form decisive factors; but its form, and the mutual position of both electrodes, must also be taken into consideration, for on these depend the distribution of the lines of force on the surface. In general, the data on the current densities and of the potentials refer to mean values; actually both are usually unlike at different points of the surface, since the number of the discharging current lines is an uneven one.

It is, therefore, often to be recommended, especially in accurate potential measurements, to "touch over" the surface. Haber<sup>1</sup> does this by shaping the siphon end of the standard electrode into a capillary tube, which he conducts along the electrode surface. If the object is to obtain tolerably equal current densities without this accurate checking of the results, the relative size and position of both electrodes must

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<sup>1</sup> Ztschr. f. phys. Chemie **32**, 209 (1900).

be taken into consideration. They may be chosen of similar dimensions and like form, and hung parallel in the bath. A better way is to choose concentric arrangements such as mentioned by Löb<sup>1</sup> and Tafel.<sup>2</sup> These electrodes consist of concentric cylinders between which the electrolysis takes place.

It has already been mentioned, in the discussion on the excess potential phenomenon, in what manner the nature of the electrode potential is of importance for the potential, leaving out of the question the changed dimensions. The evolution of hydrogen is well-nigh reversible at platinized platinum (0.005 volt excess potential); at bright (polished) platinum it is already 0.09 volt. This influence possibly occurs in a similar manner with all electrode materials. Tafel,<sup>3</sup> by reducing difficultly reducible substances in sulphuric-acid solution, was able to obtain good results only at a lead cathode, the surface of which was coated with a layer of spongy lead. Such a surface can easily be prepared by first coating the electrode anodically with a thin film of lead peroxide and then reducing this cathodically. Simultaneously a solution of the foreign metals in the surface coat is brought about by the anodic process and a *pure* lead surface obtained by reduction. Tafel, by a great number of examples, has likewise demonstrated how important it is to have a pure cathode. Even traces of impurities can decisively modify the effect. The simplest supposition is that the velocity of separation of the discharged ions is catalytically influenced by the traces of impurities. This assumption agrees best with the experimental results. Indeed, if the reduction energy is lowered by the impurities, we must conclude that an accelerated catalytical action of the hydrogen formation occurs; this agrees with the observation of Tafel, that, with a constant-current source and outer resistance, a disturbance of the reduction goes hand in hand with an increase of the current, or, what is the same thing, a lowering of the potential difference at the cathode.

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<sup>1</sup> Ztschr. f. Elektrochemie 2, 665 (1896).

<sup>2</sup> Ber. d. deutsch. chem. Gesellsch. 33, 2223 (1900).

<sup>3</sup> Ztschr. f. phys. Chem. 34, 187 (1900).

Löb and Moore<sup>1</sup> have obtained the suitable surface constitution and purity of the cathode in a different manner from Tafel. They start with a carefully platinized platinum gauze electrode and coat this electrolytically with the desired metal by electrolyzing a pure salt solution under suitable conditions. They thus succeeded, even with attackable cathodes, in obtaining quite constant cathode potentials for a long period.

Russ<sup>2</sup> has observed a peculiar influence of the pretreatment of the electrodes. If strong currents are sent through the cell for a longer period, so that an energetic evolution of hydrogen occurs in the presence of a depolarizer, the cathode potential soon drops, even if the current remains constant, and the evolution of hydrogen ceases. The original potential and renewed hydrogen evolution, after a short interruption of the current, reoccurs when the current is again turned on. Hence, the electrodes depolarize better after being charged with hydrogen than without the latter. The extent of this influence varies with different metals.

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<sup>1</sup> l. c.

<sup>2</sup> *Ztschr. f. phys. Chem.* **44**, 641 (1903).

## CHAPTER III.

### ELECTROLYSIS OF ALIPHATIC COMPOUNDS.

ORGANIC compounds which are decomposed in solution by a direct current can be divided into those that behave as electrolytes and those that act merely as depolarizers. This division is not, however, altogether appropriate, because both effects often occur simultaneously, so that a strict carrying out of this disposition is not possible without arbitrariness and numerous repetitions. The classification into oxidation and reduction processes, which proved practical in the theoretical part, would also be serviceable in the presentation of the experimental data, even though anodic and cathodic effects are sometimes observed side by side, or successively, in an electrolysis. However, the advantages of the latter division are combined with the greatest possible survey of the material if this is arranged only in accordance with the chemical character of the substances which serve as the starting-point. The sequence of the latter is prescribed by the familiar arrangement employed in text-books on organic chemistry. Moreover, the property of depolarizing, anodically or cathodically, depends upon the nature of the materials which serve as the starting-point, each group of bodies exhibiting a fixity in its electrochemical behavior, whereby an almost separate grouping of the oxidation and reduction processes naturally follows.

#### 1. CARBON AND HYDROCARBONS.

##### Carbon.

Carbon, the characteristic element of all organic compounds, is, as such, also the primal product in the electro-



synthesis of organic substances. The well-investigated electro-thermic processes of carbide formation on the one hand, and, on the other, the little explained phenomena of the electrolytic solution of carbon by the action of the anode current, form the introduction to these syntheses. That this solution occurs when carbon is used as the anode in an acid electrolyte, has been repeatedly observed; likewise the frequently occurring presence of carbon in the cathode precipitate in galvanic metal-deposition has also been noted. In the electrolysis of dilute sulphuric acid, using carbon electrodes, Bartoli and Papasogli<sup>1</sup> had found that the anode carbon is attacked, which was shown by the appearance of carbon mon- and dioxide. Coehn<sup>2</sup> then demonstrated that carbon goes into solution under suitable conditions, coloring the sulphuric acid; as a constituent part of the cation it wanders to the cathode and deposits itself, like a metal, as a conductive coating upon the platinum cathode. The nature of the solution (carbon hydroxide?) and of the precipitate has not yet been explained. Coehn<sup>3</sup> was able, however, to prove that the solution of the carbon conforms to Faraday's law and leads to the expected electrochemical equivalent  $\frac{12}{4} = 3$ .

### *Hydrocarbons.*

The great chemical resistibility of aliphatic hydrocarbons and the aggregate state of their members poor in carbon make them appear as unsuitable material for electrolytical experiments. Only the addition-reactions of unsaturated hydrocarbons offer an experimental field. This has not yet been developed. These reactions are cathodic in the addition of hydrogen, and anodic in the addition of halogens, etc. The fact that such hydrocarbons occur in the decomposition of aliphatic acids gives us an indication as to their behavior, which will be mentioned at the proper place.

<sup>1</sup> Gazz. chim. 14, 90; 15, 461 (1885); Comp. rend. 102. 363 (1886).

<sup>2</sup> Ztschr. f. Elektrochemie 2, 540, 616 (1896).

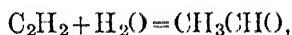
<sup>3</sup> Ibid. 3, 424 (1897).

Acetylene is the only hydrocarbon which has been used as a primal material.

**Acetylene.**—Coehn and Billitzer<sup>1</sup> have subjected acetylene to the action of the oxidizing current in alkaline and acid solution with limited anode potential. The discharging potential of oxygen, which is in the neighborhood of 1.7 volts in a pure potassium-hydroxide solution, is lowered by acetylene to 1.22 volts. At this potential a reaction begins. It is possible in the same experiment to convert the process into a quantitative one, if the tension is kept between 1.22 and 1.6 volts, a potential at which a second reaction begins, as shown by the sudden jump in the current strength. At 1.35 volts formic acid is produced exclusively, according to the following equation:



In sulphuric-acid solution the process proceeds differently. By conducting acetylene into sulphuric acid, aldehyde is first produced. This causes a depolarization of about 0.19 volt. A quantitative oxidation of the aldehyde to acetic acid occurs if the tension remains below the discharging tension of oxygen:



Nothing is as yet known regarding the reduction of acetylene and the addition of halogens.

## 2. NITRO-DERIVATIVES OF HYDROCARBONS.

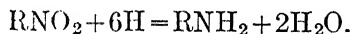
The reduction of aliphatic nitro-hydrocarbons in dilute alcoholic sulphuric-acid solution has been accomplished by Pierron.<sup>2</sup> The  $\beta$ -alkyl-hydroxylamines are obtained at platinum anodes and at a temperature of 15°–20°:



<sup>1</sup> Ztschr. f. Elektrochemie 7, 681 (1901).

<sup>2</sup> Bull. soc. chim. [3] 21, 780 (1899).

and at 70°–75° the amines:



**Nitromethane** thus yields either methylhydroxylamine or methylamine. When concentrated hydrochloric or sulphuric acid is used, hydroxylamine and formaldehyde are formed, i.e. the decomposition products of an oxime which was probably formed first:



Under similar conditions *nitroethane* is converted into  $\beta$ -ethylhydroxylamine or ethylamine; and *n-nitropropane* into  $\beta$ -n-propylhydroxylamine or n-propylamine.

### 3. HYDROXYL COMPOUNDS.

Oxidation products are principally to be expected with the aliphatic hydroxyl compounds as the lowest stage of oxidation. In fact, hydrogen is evolved unused, even if the cathode and anode are not separated by diaphragms, while the oxygen is absorbed.

**Methyl Alcohol.**—We are indebted to Renard,<sup>1</sup> Almeida and Dehérain,<sup>2</sup> Jaillard,<sup>3</sup> Habermann<sup>4</sup> and Connell<sup>5</sup> for numerous experiments on the electrolysis of methyl alcohol.

The results obtained with methyl alcohol can be summed up as follows: Hydrogen being evolved, the oxidation products formed are:

1. In aqueous sulphuric-acid solution: Methyl formate, methylal, methyl acetate, acetic acid, and methyl-sulphuric acid, a little carbon dioxide and monoxide, but no formic aldehyde.

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<sup>1</sup> Compt. rend. 80, 105, 236 (1875).

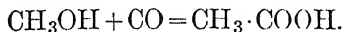
<sup>2</sup> Ibid. 51, 214 (1865).

<sup>3</sup> Ibid. 58, 203 (1863).

<sup>4</sup> Monatsch. 7, 259 (1886).

<sup>5</sup> Pogg. Ann. 36, 487 (1835).

Renard considers the formation of acetic acid as due to reciprocal action between the alcohol and carbon monoxide:



Jahn <sup>1</sup> thinks the formation must be traceable to the presence of ethyl alcohol.

2. In aqueous solution, on addition of potassium acetate (Habermann): Besides carbon dioxide and carbon monoxide, methane and potassium methyl-carbonate.

3. Without a solvent, by itself or with the addition of a little alkali: Chiefly potassium carbonate; also hydrogen, oxygen, carbon monoxide, and carbon dioxide.

While these experiments, which were carried out without giving a theoretical insight into the nature of the electrochemical reaction, yielded almost all the possible oxidation products in the oxidation of methyl alcohol, Elbs and Brunner <sup>2</sup> have discovered a method which gives 80% of the current yield in formaldehyde. This is exactly the substance which could not be proven present up to that time among the electrolytic oxidation products of methyl alcohol. Elbs and Brunner electrolyzed an aqueous solution of 160 g. methyl alcohol and 49 to 98 g. sulphuric acid in a litre. They employed a bright platinum anode in an earthenware cylinder, using a current density of 3.75 amp. and a temperature of 30°. Only traces of formic acid and carbonic acid and a little carbon monoxide, aside from the 80 per cent. of formaldehyde, were formed. Plating the platinum anode with platinum decreased the yield of formaldehyde at the expense of the carbon dioxide. With an anode of lead peroxide the carbon dioxide exceeded the aldehyde.

Dony-Hénault,<sup>3</sup> by measuring the depolarizing action of the alcohol in 3 n-sulphuric acid, found no indications of the

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<sup>1</sup> Jahn, Grundriss d. Elektrochemie 291 (1894).

<sup>2</sup> Ztschr. f. Elektrochemie 6, 604 (1900).

<sup>3</sup> Ibid., 533 (1900).

production of formaldehyde, and also obtained a negative result in an experiment.

The significance of all the conditions, for instance the acid concentration, plainly follows from the different results of the last-named investigators.

**Ethyl Alcohol.**—In the case of this alcohol the more important results have been obtained by the investigators above mentioned. Schönbein<sup>1</sup> and Becquerel,<sup>2</sup> and Bartoli and Papsogli<sup>3</sup> also later carried out some investigations on the same subject. The results of the researches are, in general, that the final products formed are the following:

1. In sulphuric acid solution: Aldehyde, acetic ester, formic ester, ethylidene oxyethyl ether ( $\text{CH}_3\text{—CH} \begin{smallmatrix} \text{OH} \\ \text{OC}_2\text{H}_5 \end{smallmatrix}$ ) (Renard), and ethyl-sulphuric acid.

2. Almeida and Dehérain state that in the electrolysis of a nitric-acid solution they observed, in addition to these oxidation products, carbonaceous derivatives of ammonia at the negative pole.

3. In hydrochloric-acid solution<sup>4</sup> chlor-acetic acids occur, in addition to the corresponding oxidation products (Riche<sup>5</sup>).

Habermann, on electrolyzing the alcohol in alkaline solution, obtained, besides carbon dioxide, an aldehyde resin (Lüdersdorf and Connel<sup>6</sup>) from which he isolated a body closely related to cinnamic aldehyde. In aqueous solution, on the addition of potassium acetate, the alcohol was split up into ethane, potassium ethyl-carbonate, carbon dioxide, and acetic ester.

Jaillard<sup>7</sup> and Riche<sup>8</sup> proved the formation of aldehyde in sulphuric- and acetic-acid solution. In hydrochloric-acid solu-

<sup>1</sup> Tommasi, *Traité d'Electrochimie* 726 (1889).

<sup>2</sup> *Compt. rend.* 81, 1002 (1875) et al. places of *Compt. rend.*; Tommasi, *Traité d'Electrochimie* 726 (1889).

<sup>3</sup> *Wiedem. Beiblätter* 7, 121 (1882).

<sup>4</sup> *Pogg. Ann.* 19, 77 (1830).

<sup>5</sup> Tommasi, *Traité d'Electrochimie* 728 (1889).

<sup>6</sup> *Pogg. Ann.* 36, 487; *Phil. Mag.* 18, 47.

<sup>7</sup> *Compt. rend.* 58, 203 (1864).

<sup>8</sup> Tommasi, *Traité d'Electrochimie* 728 (1889).

tion Lüdersdorf<sup>1</sup> obtained ester like compounds containing chlorine. Dony-Hénault<sup>2</sup> and Elbs and Brunner<sup>3</sup> have shown how to obtain certain products, depending upon definite conditions. While the former directed his aim to the anode potential, the latter sought to determine precisely the chemical factors which influence the reaction.

Dony-Hénault observed that alcohol is oxidized in sulphuric-acid solution already at an anode potential of 1.3 volts, as measured in connection with the hydrogen electrode. The oxidation of acetaldehyde, on the contrary, requires a potential of 1.66 volts to convert the aldehyde into acetic acid. Hence, the alcohol can be oxidized only to aldehyde between 1.3 and 1.66 volts. The experiment proved that, when a platinized platinum electrode is employed, only acetaldehyde is formed, and this quantitatively. The aldehyde yield decreases at a higher potential, the acid content of the electrolytes increases, and, at the same time, ethyl-sulphuric acid can be detected, as already shown by Renard. Dony-Hénault ascribes the formation of this acid to the discharge of the  $\text{SO}_4$ -ions. According to Elbs, a purely chemical action of the sulphuric acid (which becomes concentrated at the anode) on the alcohol is the more probable.

Elbs and Brunner electrolyzed an aqueous solution containing 5 g.-molecule equivalents of alcohol and 0.5-1 g.-molecule equivalent of sulphuric acid. They obtained acetaldehyde, acetic acid, and carbon dioxide, but no carbon monoxide. Acetic acid is the principal product at a bright (polished) platinum electrode. It is formed with a current yield of over 80%, the yield of aldehyde amounting to about only one twentieth of the weight of the acetic acid.

*Iodoform from Ethyl Alcohol.*—Chloroform and bromoform cannot be prepared electrolytically from alcohol (Elbs and Herz<sup>4</sup>). This is contrary to the claims of the D. R. P. No.

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<sup>1</sup> Pogg. Ann. 19, 77 (1830)

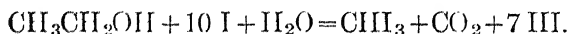
<sup>2</sup> Ztschr. f. Elektrochemie 6, 533 (1900).

<sup>3</sup> Ibid. 6, 604 (1900)

<sup>4</sup> Ibid. 4, 118 (1897).

29771 (1884). Coughlin<sup>1</sup> has substantially verified the results of Elbs in the case of bromoform. He obtained only small quantities of this body which can be easily prepared electrolytically from acetone. The formation of iodoform, on the contrary, takes place smoothly. It is obtained technically according to the above-mentioned patent. Elbs and Herz have established the following conditions for this reaction.

The course of the reaction is illustrated by the equation:



The electrolysis is best performed as follows: A solution of 13-15 g. calcined soda and 10 g. potassium iodide in 100 cc. water and 20 cc. alcohol is placed in a porous earthenware cylinder with platinum anode. The cathode, of nickel, is surrounded by a strong solution of sodium hydroxide. The electrolysis is carried out at a temperature of 70° C., with a current density at the anode of 1 amp. per 100 sq. cm., and is continued for 2-3 hours. After several hours the iodoform crystallizes out, the current yield being from 60-70 per cent. The chief by-product remaining in the mother liquor is sodium iodate.

The reduction of the iodoform by the electrolytically generated hydrogen is insignificant, according to the observations of Förster and Mewes.<sup>2</sup>

This behavior permits the discarding of the earthenware cylinder. It suffices to envelop the cathodes with parchment paper, whereby the resistance and the consumption of electrical energy is considerably diminished. The diffusion of the free alkali hydroxide away from the cathode necessitates the continuous introduction of carbonic-acid gas, because caustic alkali prevents the formation of iodoform, while carbonate promotes it. When using the covered cathodes, 20 g. calcined soda, 20 g. potassium iodide, and 50 cc. alcohol in 200 cc. water are electrolyzed at a temperature of 50°-70°, a current of carbonic-acid gas being conducted into the solution between anode and

<sup>1</sup> Am. Chem. Journ. 27, 63 (1901).

<sup>2</sup> Ztschr. f. Elektrochemie 4, 268 (1897).

cathode. The current density at the platinum anode can be from 1 to 3 amp., at the platinum cathode 4 to 8 amp., for 100 sq. cm.<sup>1</sup> The current yield is about 80%. A series of secondary reactions, which are not mentioned in the above equation, occur in this process. The hydriodic acid reacts with the soda, liberating carbonic acid and forming sodium iodide, which in turn is subject to decomposition. The iodine is converted at the anode into hypoiodite which converts the alcohol by oxidation and substitution into iodoform. Alkali-iodate is also formed by oxidation of the hypoiodite.

The reaction is the same as that involved in the usual chemical preparation of iodoform, whereby a colorless solution of hypoiodite (obtained by dissolving iodine in a sufficient quantity of potassium-hydroxide solution) is made to react with alcohol. The decomposition potential of potassium iodide, investigated by Dony-Hénault,<sup>2</sup> shows that the iodine as such does not act on the alcohol, but only after its conversion into hypoiodite. The iodine ions are set free at the same anode potential no matter if alcohol is added or not. The alcohol does not act as a depolarizer towards the iodine ion; the electrical iodoform synthesis is a typical secondary process.

*Preparation of Chloral.*—Chloral is obtained according to a process<sup>3</sup> devised by the Chemische Fabrik auf Aktien (vorm. E. Schering), if alcohol is permitted to flow into the anode chamber of the cell during the electrolysis of a potassium-chloride solution. Glucose, starch, and sugar thus also yield chloral.

Incidentally it may also be mentioned that Sand and Singer<sup>4</sup> have prepared alcohols electrolytically by reducing the mercuric-iodide compounds of alcohols. The cathode is a large sheet of platinum which is immersed in the solution of

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<sup>1</sup> Elbs, *Übungsbeispiele für die elektrolytische Darstellung chemischer Präparate* (Halle, 1902), 95.

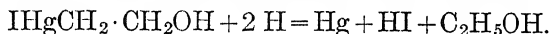
<sup>2</sup> *Ztschr. f. Elektrochemie* 7, 57 (1900).

<sup>3</sup> *Elektrochem. Ztschr.* 1, 70 (1894).

<sup>4</sup> *Ber. d. deutsch. chem. Gesellsch.* 35, 3179 (1902).

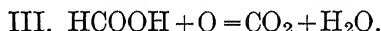
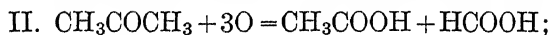
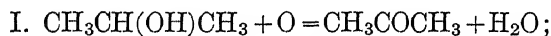


the iodide in a 10% potassium-hydroxide solution:



**Propyl Alcohol.**—*n*-Propyl alcohol offers a considerably greater resistance to electrical oxidation than methyl or ethyl alcohol, according to experiments made by Elbs and Brunner.<sup>1</sup> Propionic acid is formed as the principal product, with a current yield of over 90%, at bright (polished) and platinized platinum anodes, as well as at lead peroxide anodes when the alcohol is electrolyzed in sulphuric-acid solution. A little propionic aldehyde also occurs at lower current densities. The formation of carbon mon- and dioxides is likewise very insignificant.

**Isopropyl Alcohol**, under conditions similar to the above electrolysis of *n*-propyl alcohol, decomposes in accordance with the equations:



Acetone, acetic acid, formic acid, and carbonic acid are formed. The oxidation takes place more easily than in the case of the primary alcohols, and yields up to 70% acetone, which, however, is readily oxidized further. In alkaline electrolytes the alcohols are converted at the anode into complicated condensation products of the aldehydes.

**Isoamyl Alcohol.**—The amyl alcohol produced during fermentation was likewise exposed by Elbs and Brunner to the anodic current action in sulphuric-acid solution. It is converted into isovaleric acid with a current yield of about 80%. Some carbonic acid also formed, but isovaleric aldehyde was not present under the chosen conditions.

**Glycol.**—Of diatomic alcohols only glycol seems to have been the subject of investigation. Renard<sup>2</sup> observed in the

<sup>1</sup> Ztschr. f. Elektrochemie 6, 608 (1900).

<sup>2</sup> Ann. chim. phys. [5] 17, 303, 313 (1879); Compt. rend. 81, 188 (1875), 82, 562 (1876).

electrolysis of a sulphuric-acid solution of glycol, besides the formation of hydrogen, carbon mon- and dioxide, and oxygen, that trioxymethylene, glycolic acid, formic acid, and a substance isomeric with glucose were present in the solution.

In phosphoric-acid solution the results are similar.

**Glycerin.**—Renard<sup>1</sup> also investigated the behavior of glycerin. In the electrolysis of a dilute sulphuric-acid solution he obtained besides the gases, hydrogen, oxygen, carbon monoxide and dioxide,—trioxymethylene, formic acid, acetic acid, glyceric aldehyde, and a body to whose barium compound he gave the formula  $(C_3H_3O_4)_2Ba$  (glyceric acid?). Further electrolysis of *glyceric aldehyde* gave the ordinary oxidation products, and, as in the case of glycol, a substance closely related to ordinary glucose. Stone and McCoy<sup>2</sup> found similar results in acid solution.

Bartoli and Papasogli<sup>3</sup> repeated these experiments, varying the material of the electrodes, and obtained the following results:

Carbon anode and platinum cathode gave trioxymethylene, formic acid, glyceric acid, a substance similar to glucose, and a resin.

Graphite and platinum electrodes yielded the same products, but a larger per cent of formic acid was formed on using the latter. Mellogen was formed at the positive electrode.

Experiments on the electrolysis of glycerin in alkaline solution were made by Werther,<sup>4</sup> Renard,<sup>5</sup> Voigt,<sup>6</sup> and Stone and McCoy.<sup>7</sup> As principal products there resulted acrolein and acrylic acid, besides glyceric aldehyde or its condensation products, and glyceric acid, graphitic acid, formic acid and, according to Voigt, also propionic acid.

<sup>1</sup> Compt. rend. 81, 188 (1875), 82, 562 (1876).

<sup>2</sup> Amer. Chem. Journ. 15, 656 (1893).

<sup>3</sup> Gazz. chim. 13, 287 (1883).

<sup>4</sup> Journ. prakt. Chem. 88, 151 (1863).

<sup>5</sup> Compt. rend. 82, 562 (1876).

<sup>6</sup> Ztschr. f. angew. Chemie 107 (1894).

<sup>7</sup> Amer. Chem. Journ. 15, 656 (1893).

**Mannite.**—This hexatomic alcohol has been investigated by Renard.<sup>1</sup> Bizzarini and Campani<sup>2</sup> have published the results of an investigation on erythrite.

In the electrolyzed fluid from mannite Renard obtained formic acid, trioxymethylene, oxalic acid, a sugar isomeric with glucose, and an acid,  $C_6H_8O_8$ , which he regarded as the aldehyde of saccharic acid. He could not detect mannonic acid. Erythrite is oxidized to a great extent.

#### 4. DERIVATIVES OF THE ALCOHOLS.

**Mercaptans.**—Bunge<sup>3</sup> electrolyzed the alkali salts of ethyl and methyl mercaptans and observed the formation of disulphides at the positive pole. In the case of the sulpho-compounds, however, the free acids were generated.

**Methyl-Sulphuric Acid.**—This acid, investigated by Renard,<sup>4</sup> yielded hydrogen at the negative pole, while formic acid, carbon dioxide, carbon monoxide, and trioxymethylene, besides free sulphuric acid, were found at the positive pole.

**Potassium Trichlormethyl-Sulphate.**—This compound, electrolyzed by Bunge,<sup>5</sup> gave hydrogen and alkali at the negative pole; and at the positive pole oxygen, carbonic-acid gas, chlorine, sulphuric acid, and perchloric acid.

**Potassium Trichlormethylsulphonate.**—This salt was electrolyzed by Kolbe<sup>6</sup> in neutral concentrated aqueous solution and gave the following results:

The solution became strongly acid and contained free hydrochloric and sulphuric acids. Hydrogen was gradually evolved at the negative pole. After the decomposition was complete the solution contained potassium perchlorate, which was also observed in the case of potassium trichlormethyl-sulphate.

<sup>1</sup> Ann. chim. phys. [5] 17, 289, 316 (1879).

<sup>2</sup> Gazz. chim. 13, 490 (1883).

<sup>3</sup> Ber. d. deutsch. chem. Gesellsch. 3, 295, 911 (1870).

<sup>4</sup> Ann. chim. phys. [5] 17, 289 (1879).

<sup>5</sup> Ber. d. deutsch. chem. Gesellsch. 3, 911 (1870).

<sup>6</sup> Journ. prakt. Chem. 62, 311 (1854).

**Ethyl-Sulphuric Acid.**—Ethyl-sulphuric acid, on being subjected to electrolysis gave, according to Renard,<sup>1</sup> at the negative pole hydrogen, and at the positive pole acetic acid, some formic acid, aldehyde, and sulphuric acid. In concentrated solution a greater proportion of acetic acid was formed. The potassium salt on electrolysis breaks up, according to Hittorf,<sup>2</sup> into the ions  $K-$  and  $-OSO_2 \cdot OC_2H_5$ .

By using a diaphragm, Guthrie<sup>3</sup> obtained aldehyde and carbonic acid at the anode.

**Ethyl-Phosphoric Acid** yielded Renard<sup>1</sup> carbonic acid, aldehyde, and free phosphoric acid.

**Potassium Isoamyl-Sulphate**, according to Guthrie,<sup>3</sup> is decomposed into oxygen, valeric acid, and sulphuric acid, while

**Potassium Isoamyl-Phosphate** is split up into valeric acid and phosphoric acid.

**Potassium Isethionate** breaks up (Bunge<sup>4</sup>) into hydrogen and free acid.

## 5. ALDEHYDES, KETONES, AND THEIR DERIVATIVES.

### (a) *Aldehydes.*

Aldehydes occur as oxidation products of primary alcohols. They are readily converted into acids and give, when reduced, primary alcohols. The ketones, the oxidation products of secondary alcohols, are oxidized with difficulty. They can only be converted into acids by simultaneously splitting up the carbon chain. On being reduced they are again converted into secondary alcohols. This behavior is also apparent upon electrolysis; however, the reaction becomes more complicated as the molecule becomes more complex by an enlargement of the carbon chain and the entrance of substituents. Extensive decompositions then occur readily and the decomposition prod-

<sup>1</sup> Ann. chim. phys. [5] 17, 289 (1879).

<sup>2</sup> Pogg. Ann. 106, 530 (1859).

<sup>3</sup> Lieb. Ann. 99, 64 (1856).

<sup>4</sup> Ber. d. deutsch. chem. Gesellsch. 3, 911 (1870).

ucts, which are, naturally, often neither aldehydes or ketones, are changed further in accordance with their individual nature. Aldehydes and ketones (like the alcohols) are non-electrolytes, and act merely as depolarizers. The acids, however, which are formed by the reaction, often play a decisive part in the current conductivity, so that more thorough experiments are required in many cases to fully learn the conditions electrically dominating.

The fact that aldehydes occur among the reaction products of the alcohol electrolyses is perhaps the reason why they have rarely been chosen as the starting-point in special experiments. Considering the important rôle the aldehydes play as intermediate members of syntheses, the treatment of this subject would be highly remunerative, particularly with the aid of potential adjustments at certain values. More attention has recently been given to work on the ketones.

**Derivatives of Formaldehyde and Acetaldehyde.**—According to Tafel and Pfeffermann,<sup>1</sup> the phenylhydrazones of aldehydes are readily converted into amines by reduction in sulphuric-acid solution at a lead cathode. Thus *ethylidene phenylhydrazine* yields about 60% of the theoretical percentage of pure ethylamine salt. The decomposition of *glyoxime* is more complicated. Besides ammonia and glyoxal and a small quantity of an acid (glyoxylic acid?) there is formed as the principal product the crystalline sulphate of a base,  $C_2H_8O_2N_2$ , the nature of which could not be determined with certainty. Ethylenediamine is not formed. Nor was a diamine obtained from *methylglyoxime*.

The condensation products of aldehydes with ammonia or amido-compounds are easily reduced to amines in sulphuric-acid solution at lead cathodes. Thus *hexamethylenetetramine* yields methylamine (Knudson<sup>2</sup>); *ethylideneimine*, ethylamine; the base from acetaldehyde and ethylamine, diethylamine. Aromatic aldehydes behave similarly. The Farbwerke vorm. Meister,

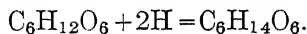
<sup>1</sup> Ber. d. deutsch. Gesellsch. **35**, 1510 (1902).

<sup>2</sup> D. R. P. No. 143197 (1902).

Lucius and Brüning<sup>1</sup> obtain the same effect in neutral or ammoniacal solution of the condensation products of fatty aldehydes with ammonia.

*Chloral Hydrate.*—Tommasi<sup>2</sup> electrolyzed a sulphuric-acid solution of chloral hydrate and was able to detect the presence of hydrochloric acid. On using diaphragms an abundance of chlorine was evolved at the anode, and acetaldehyde collected at the cathode.

*Grape Sugar.*—This sugar (investigated by Renard<sup>3</sup>) on being subjected to the action of the current broke up into carbon mon- and dioxide, formic acid, trioxymethylene, and saccharic acid. O'Brien Gunn<sup>4</sup> mentions that the aqueous glucose solution is converted by cathode reduction into mannite:



*Cane Sugar.*—On electrolyzing a concentrated solution of cane sugar, Brester<sup>5</sup> found that the solution turns strongly acid and acquires reducing properties, very little carbon dioxide being evolved. He was unable to determine the nature of the substance which he isolated by distillation, and which was free from formic and acetic acids. Continued electrolysis produced further oxidation.

The same author made some experiments on the electrolysis of dextrine, gum arabic, and collodion, but obtained no noteworthy results.

The general impression gained from these investigations is one of successive oxidation. The electrolytic oxygen gradually oxidizes the substances, the final product being carbon dioxide. Intermediate products are formed during the electrolysis, their quantity varying with the duration of the electrolysis. In following out these processes it is of especial importance immediately to withdraw the electrolyzed liquid from the action

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<sup>1</sup> D. R. P. No. 148054 (1903).

<sup>2</sup> Tommasi, *Traité d'Electrochimie* 741 (1889).

<sup>3</sup> *Ann. chim. phys.* [5] 17, 289 (1879).

<sup>4</sup> D. R. P. No. 140318 (1900).

<sup>5</sup> *Bull. soc. chim.* 8, 23 (1866).

of the current, in the manner practiced by Miller and Hofer,<sup>1</sup> by allowing the solution to flow slowly over the electrodes. Experiments of this nature have not yet been made here.

Ulsch<sup>2</sup> has made some observations on the complete electrochemical oxidation of cane sugar to carbonic acid and water. In a sulphuric acid of 1.15 sp. gr., with the addition of manganese sulphate as an oxygen-carrier, about 98% of the theoretically calculated amount of carbonic acid is obtained. The oxidation at 40°–80° in barium-hydrate solution is also fairly complete, but not directly to carbonic acid; oxalate appears also to be formed.

The apparently successful attempts at electrical purification of sugar juice, for which a large number of patents<sup>3</sup> have been taken out, may be briefly mentioned here. The gist of the various methods lies, on the one hand, in the destruction of the impurities by oxidation at the anode, and, on the other hand, in the production of precipitates which carry down colored organic substances and facilitate crystallization of the sugar by eliminating these impurities.

### b. Ketones.

**Acetone.**—Friedel,<sup>4</sup> by electrolyzing a sulphuric-acid solution of acetone, obtained carbonic acid, acetic acid, and formic acid. Mulder<sup>5</sup> and Riche<sup>6</sup> were able to isolate *mono-* and *dichloroacetone* from the hydrochloric-acid electrolyte, and *monobromoacetone* from a hydrobromic-acid solution.

These older investigations are supplemented by more recent researches with more exact results.

According to a process patented by E. Merck,<sup>7</sup> acetone is

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<sup>1</sup> Ber. d. deutsch. chem. Gesellsch. **27**, 461 (1894).

<sup>2</sup> Ztschr. f. Elektrochemie **5**, 539 (1899).

<sup>3</sup> Ibid. **1**, 251 (1894), **3**, 16 (1896); Jahrb. d. Elektrochemie **3**, 322 (1896), **8**, 628 (1901).

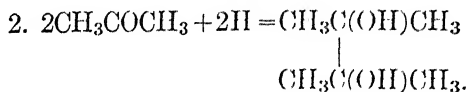
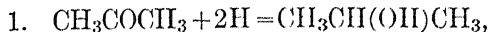
<sup>4</sup> Lieb. Ann. **112**, 376 (1859).

<sup>5</sup> Jahresb. f. Chemie **339** (1859).

<sup>6</sup> Compt. rend. **49**, 176 (1859).

<sup>7</sup> D. R. P. No. 113719 (1899).

reduced in acid and alkaline solution at a lead cathode to isopropyl alcohol and pinacone. The yields of the latter, however, are better in acid solution. About 40 parts of isopropyl alcohol and 20 parts of pinacone are obtained from 100 parts of acetone, if a sulphuric-acid electrolyte is employed. The reactions take place according to the equations:



The claims of the patent were verified by Elbs.<sup>1</sup> Elbs and Brand<sup>2</sup> publish the following details: In a 10% sodium-hydroxide solution the reduction of acetone at a lead cathode proceeds even with a low current density, hydrogen being continually liberated. The yield of isopropyl alcohol and pinacone is small; and the by-products are mesityloxide, phorone, and other condensation products. About 120 g. pure isopropyl alcohol and 60 g. pinacone hydrate were obtained in dilute sulphuric-acid solution from 300 g. acetone, lead cathodes being also used in this case. At mercury cathodes the reduction of acetone leads to a smooth conversion into isopropyl alcohol (Tafel<sup>3</sup>), without appreciable quantities of pinacone being formed. The cathode electrolyte was 40% sulphuric acid. The experiments were made by keeping the solution cool with ice.

Richard<sup>4</sup> reverts to the attempts of Mulder and Riche to prepare halogen compounds of acetone. These substitution processes occur, of course, at the anode. With a low anode current density and in concentrated hydrochloric-acid solution (3 vol. acetone to 2 vol. hydrochloric acid) monochloracetone is produced, the fluid being ice-cooled, and unattackable elec-

<sup>1</sup> Ztschr. f. Elektrochemie 7, 644 (1901). See also Elbs and Schmitz, Journ. f. prakt. Chem. 51, 591 (1895).

<sup>2</sup> Ztschr. f. Elektrochemie 8, 783 (1902).

<sup>3</sup> Ibid., 288 (1902).

<sup>4</sup> Compt. rend. 133, 878 (1901).



trodes without diaphragms employed. Monobromacetone is obtained in a similar manner, but a diaphragm and a somewhat higher temperature ( $35^{\circ}$ – $40^{\circ}$ ) are advantageous in its preparation.

*Chloroform*.—Teeple<sup>1</sup> has verified the claims of Schering's<sup>2</sup> patent as to the preparation of chloroform from acetone. The solution of the problem consisted simply in electrolyzing a solution of a chloride in the presence of acetone under conditions that would continuously give the greatest possible yield of hypochlorite. The most important conditions for this purpose are a temperature below  $25^{\circ}$ , a solution containing no alkali, or as little as possible, a high current density at the cathode, and a comparatively low one at the anode (Oettel, Förster, etc). Teeple gives the following details: In an ordinary cylinder of 150–200 cc. capacity place 100 cc. water, 20 g. sodium chloride, and 4 cc. acetone; a platinum cylinder serves as anode, and a platinum wire as cathode; close the vessel with a cork connected with a reflux condenser; cool the apparatus with running water and electrolyze, passing in a slow stream of chlorine as needed to neutralize the alkali; anode current density about 6 amp. per sq. dm. or less. After 8 to 10 hours a layer of chloroform may be removed from the bottom of the electrolyte.

The electrolysis of a calcium-chloride solution in the presence of acetone would be the best method of forming chloroform if the high resistance due to the deposits forming on the cathode could be overcome in some way.

*Bromoform*.—As already mentioned, bromoform is not formed from alcohol under the conditions which are suitable for the preparation of iodoform. It is possible, however, to convert acetone quantitatively into bromoform (Coughlin<sup>3</sup>), if acetone and potassium bromide are subjected in aqueous solution at  $25^{\circ}$  to the anodic current action and soda is gradually added. A diaphragm is used. More thorough experiments on this

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<sup>1</sup> Journ. Amer. Chem. Soc. **26**, 536 (1904).

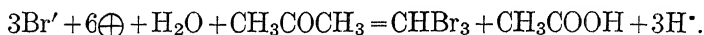
<sup>2</sup> D. R. P. 29771 (1884).

<sup>3</sup> Am. Chem. Journ. **27**, 63 (1902).

method were carried out by Müller and Loebe.<sup>1</sup> They showed that the diaphragm becomes unnecessary if a strong current of carbonic-acid gas is passed through the electrolytes kept at 15°–17°. They thus obtained a current yield of 90.2% bromoform. With a lower yield, oxidation and further bromination occurs besides the formation of bromoform. This latter takes place in stoichiometrical proportions according to the equation



or in the form of an ionic equation,



This formula is not intended to show that the acetone acts directly as a depolarizer of the bromine ion. The reaction mechanism has not yet been completely elucidated.

*Iodoform<sup>2</sup> from Acetone.*—Teepie<sup>3</sup> mentions a method by which almost the theoretical yield of iodoform can be obtained by the electrolysis of a potassium-iodide solution in the presence of acetone. No diaphragm is required, the essential feature being the gradual addition of a substance like hydrochloric acid, hydriodic acid, or, better, iodine, to neutralize the excess of potassium hydroxide as fast as it is formed. The temperature is kept below 25°, and the electrolyte thoroughly stirred; in fact the same current conditions should be observed as in the case of chloroform above mentioned, the aim in this case also being to maintain the conditions always favorable for the production of a maximum amount of hypoiodite.

**Oxidation of Ketoximes.**—According to an investigation made by J. Schmidt,<sup>4</sup> ketoximes, on electrolysis in dilute sulphuric-acid solution, are decomposed in such a way that pseudonitroles are formed besides other nitroso-compounds. If *acetoxime* is oxidized at a temperature not over 10° in a 2%

<sup>1</sup> Ztschr. f. Elektrochemie 10, 409 (1904).

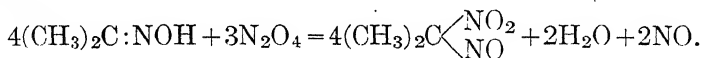
<sup>2</sup> See also p. 60.

<sup>3</sup> Journ. Amer. Chem. Soc. 26, 170 (1904).

<sup>4</sup> Ber. d. deutsch. chem. Gesellsch. 33, 871 (1900).

sulphuric-acid solution, using a platinum anode, and an earthenware cell as diaphragm, the anode fluid is soon colored blue; at the same time a white crystalline substance is precipitated upon the anode. This substance is propylpseudonitrole,

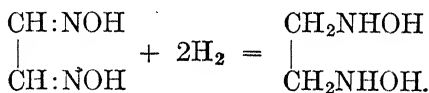
$(\text{CH}_3)_2\text{C} \begin{smallmatrix} \diagup \text{NO}_2 \\ \diagdown \text{NO} \end{smallmatrix}$ . This was formed perhaps in the following manner:



A part of the acetoxime will split up upon electrolysis, oxides of nitrogen being given off, and these latter in the nascent state will convert any unchanged acetoxime into propylpseudonitrole. A blue nitroso-compound can be isolated from the anode solution. A diaphragm is unnecessary in these experiments. *Diethylketoxime* and *methylethylketoxime* behave just like acetoxime.

Isopropylamine is formed in the reduction of acetoxime in sulphuric-acid solution at a lead cathode (Tafel and Pfeffermann<sup>1</sup>). This process is a general one. The electrolytic reduction of ketoximes leads, like that of the aldoximes and phenylhydrazones, to the final formation of amines. About 66% of the theoretically possible quantity of isopropylamine is formed from acetoxime; *acetonphenylhydrazone* gives about the same yield.

*Glyoxime*,  $\text{OHN}=\text{CH}:\text{CH}:\text{NOH}$ , under similar conditions, yields, as the chief product (about 60% yield) a substance whose reactions probably characterize it as  $\beta$ -ethylenedihydroxyamine:

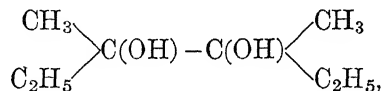


The electrolyte also contains ammonia, glyoxal, and small quantities of acid (glyoxalic acid).

<sup>1</sup> Ber. d. deutsch. chem. Gesellsch. **35**, 1510 (1902); see also D. R. P. No. 141346 (1902).

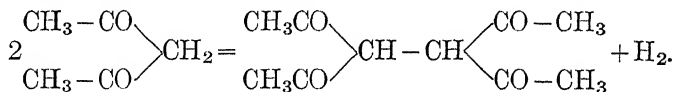
*Isonitrosoacetone*. — Ahrens and Meissner<sup>1</sup> electrolyzed isonitrosoacetone,  $\text{CH}_3\text{COCHNOH}$ , in sulphuric-acid solution to obtain amidoacetone. However, a poor yield of dimethylpyrazine,  $\text{C}_6\text{H}_8\text{M}_2$  (ketine) was obtained.

*Methylethylketone*. — This substance, reduced at a lead cathode in the same manner as acetone by Elbs and Brand,<sup>2</sup> gives very unfavorable results in alkaline solution. In sulphuric-acid solution, although the yield is insufficient, there were obtained the modification of methylethylpinacone melting at  $50^\circ$ ,



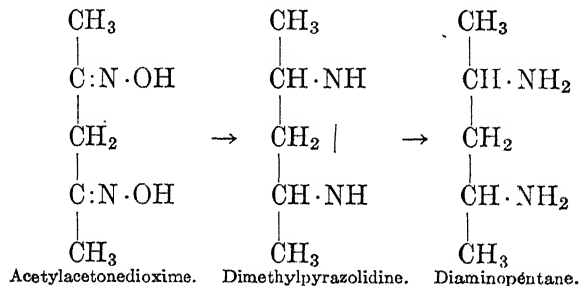
and secondary butyl alcohol,  $\text{CH}_3\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{CH}_3$ .

*Acetylacetone*. — This is said to pass, in alcoholic solution, into tetracetylene (Mulliken<sup>3</sup>):



The substance therefore breaks up into  $\text{H}^+$  and  $(\text{CH}_3\text{CO})_2\text{CH}^-$ ; the anions unite at the anode to the resulting compound.

*Acetylacetondioxime*, in a 30% sulphuric acid at a lead cathode, is converted into dimethylpyrazolidine and 2,4-diaminopentane (Tafel and Pfeffermann<sup>4</sup>).



Pyrazolidine is the chief product.

<sup>1</sup> Ber. d. deutsch. chem. Gesellsch. **30**, 532 (1897).

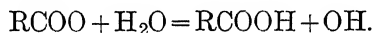
<sup>2</sup> Ztschr. f. Elektrochemie **8**, 786 (1902).

<sup>3</sup> Amer. Chem. Journ. **15**, 323 (1893).

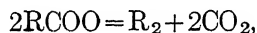
<sup>4</sup> Ber. d. deutsch. chem. Gesellsch. **36**, 219 (1903).

## 6. ACIDS.

While the substances thus far discussed are active only as depolarizers, but not as electrolytes, the conditions are different in the case of acids and their salts. These are primarily electrolytes; their ions take care of the current conductivity and are first separated or brought into reaction at the electrodes. In general, hydrogen ions are discharged at the cathode when acids form the electrolyte, and metal ions in the case of salts; acid-radical ions are discharged at the anode. The latter have the form  $\text{RCOO}$  and are subject to a series of reaction possibilities. By reacting with water the acid is again regenerated, oxygen being evolved.



Often, however, two anions unite, carbon dioxide being split off:



wherein, if R is a hydrocarbon radical, like methyl, ethyl, etc., hydrocarbons are formed having double the number of carbon atoms contained in the radicals united with the carboxyl group. Thus ethane is synthesized from acetic acid. This simple form of reaction is often not the predominating one, which will be explained more fully under the separate substances.

An acid can often develop acid properties at other than the carboxyl groups, e.g. hydroxyl and methylene groups. In that case there must occur the corresponding ions which are able to direct the reaction in entirely different channels from those mentioned. Thus, as is well known, the methylene group placed between two carboxyl or ester groups is capable of forming salts. Such salts as, for instance, sodium diethylmalonic ester, behave, on electrolysis, in a manner analogous to that of the salts of carboxylic acids. By determining their conductivities, Ehrenfeld<sup>1</sup> has recently proved that the

<sup>1</sup> Ztschr. f. Elektrochemie 9, 335 (1903).

methylene groups of succinic acid, malonic acid, and glutaric acid are capable of forming hydrogen ions.

The first successful experiments in the electrolysis of aliphatic carboxylic acids were made by Kolbe.<sup>1</sup> These experiments are supplemented by the researches of Kekulé,<sup>2</sup> Brown and Walker,<sup>3</sup> Mulliken,<sup>4</sup> and Weems,<sup>5</sup> who amplified our knowledge regarding this subject which, still further investigated in the most varied directions by a number of investigators, has yielded valuable results.

**Carbonic Acid.**—Carbonic acid deserves mention here because it can be converted electrolytically into formic acid. Royer<sup>6</sup> observed its formation at zinc and zinc-amalgam electrodes in the electrical reduction of carbonic acid dissolved in water, a current of the gas being conducted through the latter during electrolysis. Klobukow<sup>7</sup> was likewise able to prove the presence of formic acid in water which was electrolyzed and through which a current of carbonic-acid gas was passed.

Lieben<sup>8</sup> has made extensive experiments on the reductivity of carbonic acid. He obtained formic acid as the sole reduction product of carbonic acid. The supposition of Bach<sup>9</sup> that formaldehyde must also be formed is false. The formation of formaldehyde was never proved. Quite recently Coehn and Jahn<sup>10</sup> have shown that formic acid is the only tangible reduction product. They succeeded in obtaining quantitative current yields, using carefully prepared amalgated zinc electrodes, as already previously employed by Royer, and using a cold saturated potassium-sulphate solution as electrolyte. According to Constam and Hansen,<sup>11</sup> potassium

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<sup>1</sup> Lieb. Ann. **69**, 257 (1849), **113**, 244 (1860).

<sup>2</sup> Ibid. **131**, 79 (1864).

<sup>3</sup> Ibid. **261**, 107 (1891), **274**, 41 (1893).

<sup>4</sup> Amer. Chem. Journ. **15**, 523 (1893).

<sup>5</sup> Ibid. **16**, 569 (1894).

<sup>6</sup> Compt. rend. **70**, 731 (1870).

<sup>7</sup> Journ. f. prakt. Chem. [2] **34**, 126 (1887).

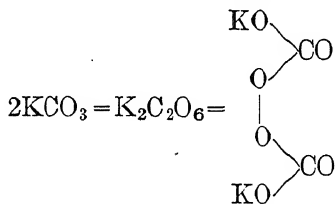
<sup>8</sup> Monatshefte f. Chem. **16**, 211 (1895), **18**, 582 (1897).

<sup>9</sup> Compt. rend. **126**, 479 (1898).

<sup>10</sup> Ber. d. deutsch. chem. Gesellsch. **37**, 2836 (1904).

<sup>11</sup> Ztschr. f. Elektrochem. **3**, 137 (1896), **3**, 445 (1897).

percarbonate is formed when a saturated solution of potassium carbonate is electrolyzed at  $-10^{\circ}$  to  $-15^{\circ}$ , particularly at a high current density, the anions  $\text{KCO}_3$  uniting when set free:

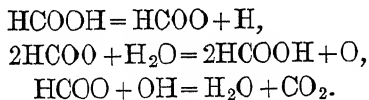


The potassium salt is precipitated as a blue powder. It has not been possible to isolate other salts and free percarbonic acid. The experiments of Salzer,<sup>1</sup> however, indicate that the free acid may occur perhaps intermediately. He proved the presence of active oxygen in a solution of potassium bicarbonate through which was passed a continuous current of carbonic-acid gas.

#### 1. MONOBASIC ACIDS, $\text{C}_n\text{H}_{2n}\text{O}_2$ .

**Formic Acid.**—This acid and its salts have been the subjects of thorough electrolytic investigations. These were carried out chiefly by Brester,<sup>2</sup> Renard<sup>3</sup> and Bourgoin,<sup>4</sup> Bartoli and Papasogli,<sup>5</sup> Jahn,<sup>6</sup> etc.

The progress of the decomposition is accompanied by the evolution of carbon dioxide and oxygen at the positive pole and hydrogen at the negative pole. The quantitative relations of the decomposition products vary with the concentration of the solution and the density of the current. The reactions occur according to the following equations:



<sup>1</sup> Ztschr. f. Elektrochem. 8, 902 (1902).

<sup>2</sup> Ztschr. f. Chem. 60 (1866).

<sup>3</sup> Ann. chim. phys. [5] 17, 289 (1878).

<sup>4</sup> Ibid. [4] 14, 157 (1868).

<sup>5</sup> Gazz. chim. 13, 22, 28 (1883).

<sup>6</sup> Wied. Ann. (N. F.) 37, 408 (1889).

It is therefore theoretically impossible to effect the complete decomposition of the formic acid present. In the electrolysis of sodium formate, carbon dioxide and formic acid are in fact always formed at the positive pole and hydrogen and sodium hydroxide at the negative pole.

A splitting up of the anions  $\text{HCOO}$  into  $\text{H}$  and  $\text{CO}_2$  at the anode does not occur, since the oxidizing hydroxyl ions split off the hydrogen as water (Hofer and Moest <sup>1</sup>). The discussion of the other salts is unnecessary since their behavior is quite analogous.

The dependence of the decomposition of formic acid upon the conditions of the experiment has been investigated by Petersen <sup>2</sup> and Salzer.<sup>3</sup>

Petersen found that, if the solution was concentrated, the current strength exercised only a trifling influence on the decomposition phenomena in the electrolysis of sodium formate. According to Salzer's researches, formic acid in sulphuric-acid solution cannot completely suppress the evolution of oxygen at a platinized anode. Sodium formate is for the most part converted into carbonate; in neutral solution small quantities of percarbonate are also formed.

*Formic ester* in sulphuric-acid solution is attacked only with difficulty in the cathode chamber (Tafel and Friedrichs <sup>4</sup>); acetic ester, cyanacetic ester, and phenylacetic ester, it may be remarked here, are not attacked at all.

### Acetic Acids.

**Acetic Acid.**—Glacial acetic acid is a poor conductor of electricity. According to Lapschin and Tichanowitsch,<sup>5</sup> its decomposition when effected by 900 Bunsen elements yields at the anode carbon mon- and dioxide, and at the cathode carbon

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<sup>1</sup> Lieb. Ann. **323**, 284 (1902).

<sup>2</sup> Ztschr. f. phys. Chem. **33**, 106 (1900).

<sup>3</sup> Ztschr. f. Elektrochemie **8**, 893 (1902).

<sup>4</sup> Ber. d. deutsch. chem. Gesellsch. **37**, 3187 (1904).

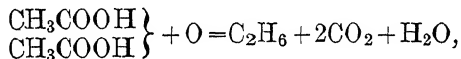
<sup>5</sup> Neue Peters. Acad. Bull. **4**, 81 (1861).



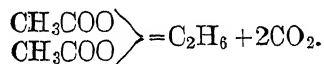
and a small quantity of a gas the nature of which was not established.

Bourgoin,<sup>1</sup> on electrolyzing the dilute acid, observed hydrogen at the negative pole and oxygen, carbon dioxide, and traces of carbon monoxide at the positive pole.

The reactions involved in the decomposition of the *alkali salts* are more interesting. Kolbe,<sup>2</sup> on decomposing a concentrated solution of potassium acetate, obtained a hydrocarbon in addition to other decomposition products. According to the idea then prevailing, acetic acid underwent oxidation in the sense that it was thereby changed into carbon dioxide and methyl, both of which appeared at the positive pole, while at the negative pole only hydrogen was evolved, and a part of the methyl was oxidized to methyl oxide. The hydrocarbon evolved was in fact ethane, which always accompanies the decomposition of potassium-acetate solutions, while the other decomposition products formed vary with the density of the electric current and the temperature of the solutions. Thus Kolbe identified methyl ether and methyl acetate in the solution, while Bourgoin observed no decomposition products other than carbon monoxide and dioxide. Jahn,<sup>3</sup> who employed currents of very low electrode density, obtained by the electrolysis of an almost saturated solution of sodium acetate only carbon dioxide, ethane, and hydrogen. The formation of ethane can be explained by assuming either the direct oxidation of the acetic acid,



or the decomposition of the anion,



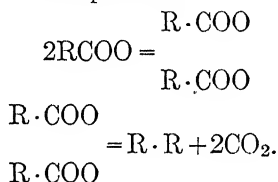
<sup>1</sup> Ann. chim. phys. [4] 14, 157 (1868).

<sup>2</sup> Lieb. Ann. 69, 279 (1849).

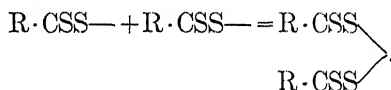
Grundriss d. Elektrochemie (1895), 292.

Kekulé<sup>1</sup> advanced a theory based upon the phenomena of decomposition, and from this deduced certain formulæ which make it possible to predict the nature of the products resulting from the electrolysis of monobasic and dibasic acids of the fatty-acid series. Since, however, the reaction is influenced by the slightest variation of conditions, his formulæ hold good only in the case of the decomposition of perfectly pure substances, a condition seldom met with in practice.

Löb<sup>2</sup> is in favor of accepting in certain cases the theory advanced by Kekulé, who sought by experiments to prove the intermediate formation of the anhydride, while Schall<sup>3</sup> assumes the formation of an acid superoxide:



This conclusion is drawn from the observed fact that the dithionic acids, on the electrolysis of their alkali salts, actually give acid supersulphides which correspond with the superoxides:



In contrast to the acid superoxides, the acid supersulphides are stable compounds.

Bourgoin draws the following conclusions from his experiments: He considers the intermediate anhydride formation as the most important process in the electrolysis of organic acids; this brings about the secondary oxidation processes, oxygen being given off. He also considers as secondary reactions the transition from the acid anhydride to the hydrate with the taking up of water, and the oxidation of acids by the oxygen derived from the acid itself. This explanation agrees

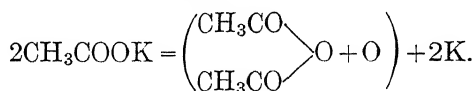
<sup>1</sup> Lieb. Ann. **131**, 70 (1864).

<sup>2</sup> Ztschr. f. Electrochemie **3**, 43 (1896).

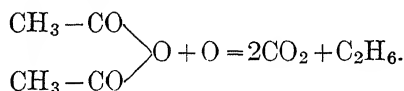
<sup>3</sup> Ibid. **3**, 83 (1896).

with the fact that water is a weak electrolyte and serves principally as a dissociating medium. The typical processes in the electrolysis of acetic acid are hence the following:

Electrolytic decomposition:



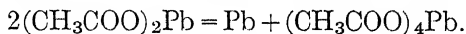
Characteristic oxidation:



Kolbe and Kämpf,<sup>1</sup> on electrolyzing a concentrated potassium-acetate solution, obtained at the anode acetic methyl ester, formic methyl ester, ethane, ethylene, and carbon dioxide; and at the cathode hydrogen and potassium hydroxide. In an alkaline solution of the salt Bourgoin<sup>2</sup> obtained, amongst other products, sodium formate (by reduction of the carbonic acid); but so far as hydrocarbons were concerned he could only prove the presence of ethane and ethylene.

Besides the alkali salts, the copper, lead, manganese, and uranium salts were subjected to electrolysis by Dupré,<sup>3</sup> Wiedemann,<sup>4</sup> Despretz,<sup>5</sup> and Smith.<sup>6</sup> The metals were precipitated on the cathode, a portion of the manganese and lead in the form of superoxides.

Elbs,<sup>7</sup> by the electrolysis of lead diacetate in glacial-acetic-acid solution, obtained at the anode crystallized lead tetracetate:



Fused potassium acetate, according to the experiments of Lassar-Cohn,<sup>8</sup> yields at the cathode methane, hydrogen, and

<sup>1</sup> Journ. prakt. Chem. [2] 4, 46 (1871).

<sup>2</sup> Ann. chim. phys. [4] 14, 157 (1868).

<sup>3</sup> Arch. d. scienc. phys. et. nat (Geneva) 35, 998 (1871).

<sup>4</sup> Poggend. Ann. 104, 162 (1858).

<sup>5</sup> Compt. rend. 45, 449 (1857).

<sup>6</sup> Amer. Chem. Journ. 7, 329 (1885). Electrochemical Analysis (Smith), p. 94.

<sup>7</sup> Ztschr. f. Elektrochemie 3, 70 (1896).

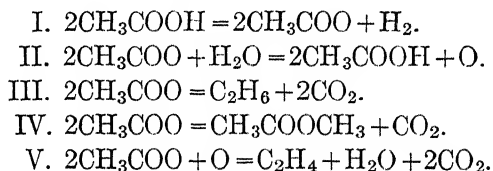
<sup>8</sup> Lieb. Ann. 251, 358 (1889).

carbon; at the anode carbon dioxide. This result has recently been substantiated by Berl,<sup>1</sup> who also proved by special experiments that this decomposition is the result of the action of the potassium, set free cathodically, on the fused potassium acetate.

Very careful and comprehensive experiments on the electrolysis of the alkali salts of organic acids have very recently been made by Petersen.<sup>2</sup> The latter made exact analyses of the gases occurring at the electrodes and thereby obtained an insight into the quantitative course of the reactions, and determined their nature.

Petersen<sup>3</sup> was enabled to wholly confirm the earlier statements regarding the electrolysis of acetic acid by Murray,<sup>4</sup> who investigated the influence of the concentration, current strength, and temperature upon the course of the electrolysis and found, like earlier investigators, carbonic acid, oxygen, hydrogen, ethane, and methyl acetate. Murray disputes only the occurrence of ethylene which Kolbe and Kämpf declare they found.

Petersen, however, clearly proved the presence of the latter in small quantities, and expressed the decomposition of acetic acid by the following equations:



In general, equations I and III predominate; V is always only traceable.

Hofer and Moest<sup>5</sup> report upon the formation of alcohols in the electrolysis of salts of fatty acids.

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<sup>1</sup> Ber. d. deutsch. chem. Gesellsch. **37**, 325 (1904).

<sup>2</sup> Ztschr. f. phys. Chem. **33**, 90, 295, 698 (1900).

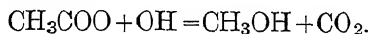
<sup>3</sup> Ibid. 108 (1900).

<sup>4</sup> Journ. of the Chem. Soc. **61**, 10 (1892).

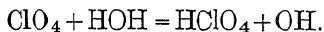
<sup>5</sup> Lieb. Ann. **323**, 284 (1902). D. R. P. No. 138442 (1901).

They found that copious quantities of methyl alcohol, but no perchloric acid esters, were produced by the electrolysis of a mixture of sodium acetate and sodium perchlorate. The reaction takes place in the same manner as in the case of some homologues of acetic acid, and it was found that an addition of alkali sulphate or carbonate acts like the perchlorate.

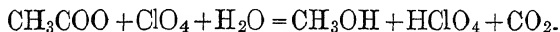
The general nature of the reaction is that the carboxyl group is replaced by hydroxyl, so that an alcohol is formed having one carbon atom less than the acid; thus methyl alcohol is obtained from acetic acid:



The hydroxyl ion can be derived from the water, or be formed in the regeneration of the inorganic acid acting as electrolyte:



The formation of methyl alcohol can hence be formulated as follows:



If the electrolysis is carried out between platinum electrodes without diaphragms but with continual stirring, up to 90% of the theoretical yield of methyl alcohol can be obtained from acetic acid and the above-mentioned inorganic salts.

The method can also be employed in the preparation of formaldehyde, since the methyl alcohol on further oxidation is converted into formaldehyde (see p. 58).

Quite recently Förster and Piguet<sup>1</sup> have investigated the electrolysis of potassium acetate, using various anodes. In the earlier experiments polished platinum had served as the anode. Iridium gives the same results as platinum; with iron and palladium anodes, however, not a trace of ethane is formed, but essentially an evolution of oxygen occurs besides the oxidation of the acetic acid to carbon dioxide. At platinized platinum electrodes there occurs, depending upon the current tension, either an evolution of oxygen and oxidation to carbonic acid (no ethane being formed), or ethane is produced, with

<sup>1</sup> Ztschr. f. Elektrochemie 10, 729 (1904).

very little evolution of oxygen and a very considerable oxidation of the acetic acid to carbon mon- and dioxide.

Förster and Piguet recognize three processes:

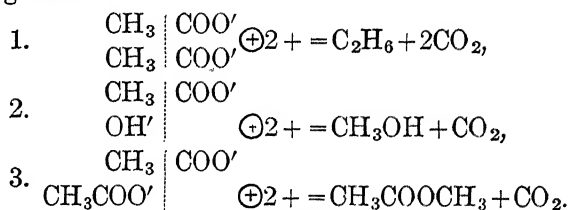
1. Evolution of oxygen.
2. Oxidation of the acetic ester formed to carbon dioxide or carbon monoxide.
3. Formation of ethane.

They find that the anode potential determines the effect. The first reaction, which occurs predominately at iron and palladium electrodes, requires the lowest potential. With platinized platinum electrodes the potential lies higher; the oxidation action can exceed the evolution of oxygen; and with a particularly high potential, which is obtained by prepolarizing the platinized anode,<sup>1</sup> ethane is produced. With polished platinum and iridium anodes the potential is still higher than with prepolarized platinized platinum anodes. Thus the production of ethane predominates over the oxidation of acetic ester.

Regular fluctuations of the anode potential, which often occur in electrolysis, seem to point to the formation of transition resistances by intermediately occurring phases of poor conductivity (acetic acid, acetic anhydride).

The presence of free alkali is always injurious to the production of ethane. The evolution of oxygen at platinized platinum increases with increasing alkalinity and decreases at polished anodes, while the oxidation of acetic ester increases.

Hofer and Moest<sup>2</sup> call attention to the great part which the production of the methyl alcohol demands in the oxidation effects, and which Förster and Piguet have neglected to point out. They formulate the principal processes in the following manner:



<sup>1</sup> S. Friessner, *Zeitschr. f. Elektrochem.* 10, 270 (1904).

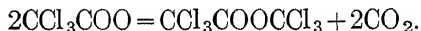
<sup>2</sup> *Ztschr. f. Elektrochem.* 10, 833 (1904).

An impartial decision has not yet been given as to whether the ethane production depends upon a direct union of the anions or upon the oxidation of an intermediate product, like acetic acid, acetic anhydride, or acetyl superoxide.

*Monochloroacetic Acid*, according to Kolbe,<sup>1</sup> is reduced to acetic acid, hydrochloric acid being split off; at the same time free chlorine is evolved (Bunge<sup>2</sup>).

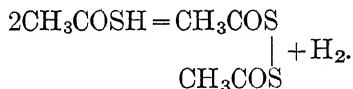
*Sodium Dichloroacetate* yields, besides carbon mon- and dioxide and oxygen, a very easily decomposable oil containing chlorine, whose nature has not yet been made clear. (Troeger and Ewers.<sup>3</sup>)

*Trichloroacetic Acid* was electrolyzed by Elbs and Kratz<sup>4</sup> as sodium or zinc trichloroacetate. Trichloroacetic trichloromethyl ester was formed:



*Potassium Cyanacetate*.—With this Moore<sup>5</sup> obtained at the positive pole carbon dioxide, besides traces of nitrogen and ethylene cyanide; at the negative pole hydrogen and potassium hydroxide, bodies analogous to those obtained in the decomposition of sodium acetate.

*Thioacetic Acid*.—On electrolysis this gives acetyl disulphide at the anode (Bunge<sup>6</sup>):



<sup>1</sup> Lieb. Ann. **69**, 279 (1849).

<sup>2</sup> Journ. russ. chem. Gesellsch. **1**, 690 (1892); see also Troeger and Ewers, Journ. f. prakt. Chem. **58**, 121 (1898).

<sup>3</sup> Journ. f. prakt. Chem. **58**, 121 (1898).

<sup>4</sup> Ibid. [2] **55**, 502 (1897).

<sup>5</sup> Ber. d. deutsch. chem. Gesellsch. **4**, 519 (1871).

<sup>6</sup> Ibid. **3**, 297 (1870).

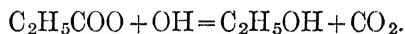
### Propionic Acids.

**Propionic Acid.**—The electrolysis of a concentrated solution of sodium propionate was carried out by Jahn<sup>1</sup> and, when density of the currents employed was not too great, yielded hydrogen, ethylene, and carbon dioxide, but little butane, the quantity of which further decreased when the electrolyte was diluted. This result Petersen<sup>2</sup> confirmed. The evolution of oxygen increases as the butane yield decreases. The amount of ethylene increases with increased dilution up to a maximum, which is reached at a concentration of the electrolyte corresponding to about 14% potassium propionate. On further dilution it again decreases. Petersen<sup>2</sup> also found that ethyl propionate is always produced, corresponding to the analogous process in the case of acetic acid. He expresses the course of the electrolysis by the following equations:

- I.  $2\text{C}_2\text{H}_5\text{COOH} = 2\text{C}_2\text{H}_5\text{COO} + \text{H}_2$ .
- II.  $2\text{C}_2\text{H}_5\text{COO} + \text{H}_2\text{O} = 2\text{C}_2\text{H}_5\text{COOH} + \text{O}$ .
- III.  $2\text{C}_2\text{H}_5\text{COO} = \text{C}_4\text{H}_{10} + 2\text{CO}_2$ .
- IV.  $2\text{C}_2\text{H}_5\text{COO} = \text{C}_2\text{H}_5\text{COOC}_2\text{H}_5 + \text{CO}_2$ .
- V.  $2\text{C}_2\text{H}_5\text{COO} + \text{O} = 2\text{C}_2\text{H}_4 + \text{H}_2\text{O} + 2\text{CO}_2$ .

Miller and Hofer<sup>3</sup> have been successful in introducing iodine into propionic acid by electrolyzing an aqueous solution of sodium propionate and potassium iodide.

Ethyl alcohol can be obtained in small quantity from sodium propionate and sodium perchlorate in concentrated solution (Hofer and Moest<sup>4</sup>) in the same manner as methyl alcohol and formaldehyde are formed from acetic acid and perchlorate:



<sup>1</sup> Wied. Ann. (N. F.) **37**, 430 (1889); see also Bunge: Chem. Centralblatt **1**, 382 (1890).

<sup>2</sup> Ztschr. f. phys. Chem. **33**, 110 (1900).

<sup>3</sup> Ber. d. deutsch. chem. Gesellsch. **28**, 2436 (1895).

<sup>4</sup> Lieb. Ann. **323**, 284 (1902).



Acetaldehyde is formed as the oxidation product of the latter.

*Sodium α-Dichloropropionate* behaves analogously to sodium trichloroacetate (Troeger and Ewers<sup>1</sup>). There is formed, besides carbonic acid and oxygen, the crystalline α-dichloropropionic α-dichlorethyl ester:



*Sodium β-iodopropionate*, according to the last-named investigators, yields a little iodoform besides iodine; the gases formed are principally carbonic acid. Carbon monoxide and oxygen occur only in small quantity.

#### Butyric Acids.

**Butyric Acids.**—The two butyric acids were electrolyzed by Bunge.<sup>2</sup> With isobutyric acid it was not possible to obtain hexane, but the normal acid yielded some butane besides larger quantities of propylene.

Careful and reliable investigations on the electrolysis of the potassium salts of *butyric and isobutyric acids* have been published by M. F. Hamonet.<sup>3</sup> His apparatus consisted of a copper beaker 23 cm. high and 8 cm. in diameter, which served as the cathode. A porous earthenware cell, which contained the anode and was closed with a three-hole stopper, stood in the beaker. The perforations in the stopper held a thermometer, a gas-delivery tube, and the electric conductor leading to the anode. The anode used in some experiments was a platinum wire 1 mm. in diameter and 2 m. in length; in others a platinum cylinder 14 cm. high and 2.5 cm. in diameter. This variation of current density was, however, of secondary importance. Solutions of the potassium salts having a specific gravity of 1.08–1.19 were used as the electrolyte. Current strengths of 4–5 amp. were reached with a difference of potential at the poles of 6–9 volts. The electrolysis was continued 2–3 hours,

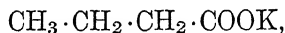
<sup>1</sup> Journ. f. prakt. Chem. 53, 121 (1893).

<sup>2</sup> Journ. f. russ. phys. Gesellsch. 21, 525 (1889).

<sup>3</sup> Comp. rend. 123, 252 (1896).

the solution being kept cool. The following results were obtained:

*Potassium Butyrate,*



yielded 225 g. propylene bromide ( $\text{CH}_3 \cdot \text{CHBr} \cdot \text{CH}_2\text{Br}$ ), corresponding to 47 g. propylene ( $\text{CH}_2 = \text{CH} \cdot \text{CH}_2$ ); 18 gr. isopropyl alcohol ( $\text{CH}_3 \cdot \text{CHOH} \cdot \text{CH}_3$ ); 4.5 g. butyric isopropyl ester ( $\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{COOCH}(\text{CH}_3)_2$ ); and 4.5 g. complicated products, which became resinous when the ester was saponified by boiling with alkali hydroxide. Hexane ( $\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_3$ ), and propyl alcohol ( $\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2\text{OH}$ ) could not be detected. They could, therefore, have been formed only in trifling quantity.

The very remarkable formation of isopropyl alcohol can only be explained by assuming the hydration of propylene or the molecular rearrangement of the group  $\text{CH}_3\text{CH}_2\text{CH}_2-$ .

*Potassium Isobutyrate,*

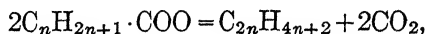


This salt gave 300 g. propylene bromide ( $\text{CH}_3 \cdot \text{CHBr} \cdot \text{CH}_2\text{Br}$ ) equivalent to 62. g propylene ( $\text{CH}_3 \cdot \text{CH} \cdot \text{CH}_2$ ); 26 g. isopropyl alcohol,  $(\text{CH}_3)_2 \cdot \text{CH} \cdot \text{OH}$ ; over 12 g. isobutyric isopropyl ester,  $(\text{CH}_3)_2 \cdot \text{CH} \cdot \text{COO} \cdot \text{CH} : (\text{CH}_3)_2$ ; and 6 g. of an oil having a pepper-like odor and boiling at  $130^\circ$ – $150^\circ$ .

In this case also the paraffin isohexane  $(\text{CH}_3)_2 \cdot \text{CH} \cdot \text{CH} : (\text{CH}_3)_2$  was not formed.

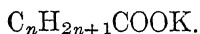
Hamonet draws the following conclusions from these results:

1. The equation

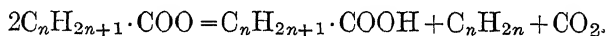


representing the reaction in the electrolysis of the alkali salts of the fatty acids, which since the experiments of Kolbe has been almost universally accepted, can no longer claim to represent the truth in the case, since no or almost no paraffins result from this operation.

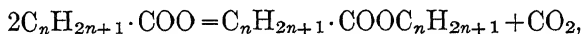
2. The olefine  $C_nH_{2n}$  sometimes predominates among the products formed by the electrolysis of the alkali salts of the fatty acids,



The general nature of the reactions is represented by the following equation:



3. An alcohol with  $n$  carbon atoms is always formed if the acid contains  $(n+1)$  carbon atoms. The structure of the alcohol is not always that which is expected. Frequently more than a third of the energy of the current is expended in the formation of the alcohol. Whether the alcohol is generated by the saponification of the ester present, according to the equation

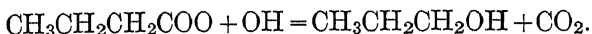


or whether it is formed by the hydration of the olefines,  $C_nH_{2n} + H_2O = C_nH_{2n+1}OH$ , is still uncertain. (Compare the explanation of Hofer and Moest, p. 84.)

A more thorough investigation of the substances resulting from the electrolysis of compounds possessing higher molecular weights is yet wanting.

Petersen<sup>1</sup> was able to obtain n-hexane and propyl butyrate in small quantity from butyric acid; from isobutyric acid he got diisopropyl (isohexane) in addition to the products observed by Hamonet.

If butyric acid is electrolyzed with perchlorate, according to the procedure of Hofer and Moest,<sup>2</sup> hexane is the preponderating product; there are also obtained propyl alcohol and its oxidation product, propionic aldehyde:

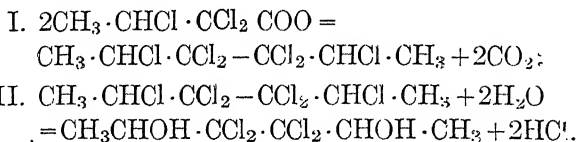


<sup>1</sup> Bull. d. l'Acad. roy. de Danemark (1897) 397; Ztschr. f. phys. Chem. **33**, 115 (1900).

<sup>2</sup> l. c.

Isobutyric acid yields, accordingly, isopropyl alcohol and acetone.

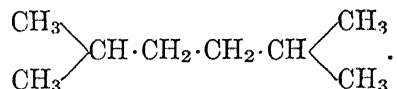
*Trichlorobutyric Acid*.—According to Troeger and Ewers,<sup>1</sup> a tetrachlorhexyleneglycol is formed at the anode from sodium  $\alpha\alpha\beta$ -trichlorobutyrate. The authors assume the following equations from this process:



Accordingly, a hexachlorhexane would be first formed in a normal manner,  $\text{CO}_2$  being split off; secondarily, the two very mobile  $\beta$ -chlorine atoms would be torn away by water, hydrochloric acid and tetrachlorhexyleneglycol resulting.

#### Valeric Acids.

*Valeric Acids*.—Kolbe<sup>2</sup> electrolyzed the potassium salt of *isovaleric acid* in concentrated aqueous solution and obtained as chief product octane (dissobutane):



Besides this there appeared as decomposition products hydrogen, carbonic acid, butylene, and the butyl ester of valeric acid.

Brester,<sup>3</sup> who performed his experiments under different conditions, obtained at the anode a gaseous mixture of carbon dioxide, butylene, and oxygen.

Petersen<sup>4</sup> subjected the behavior of both acids to a thorough investigation. He established the formation of normal octane and butyl valerate in the decomposition of *n-valeric acid*; among

<sup>1</sup> Journ. f. prakt. Chem. **59**, 464 (1899).

<sup>2</sup> Lieb. Ann. **69**, 257 (1849).

<sup>3</sup> Jahresb. f. Chem. **86** (1859), 757 (1866).

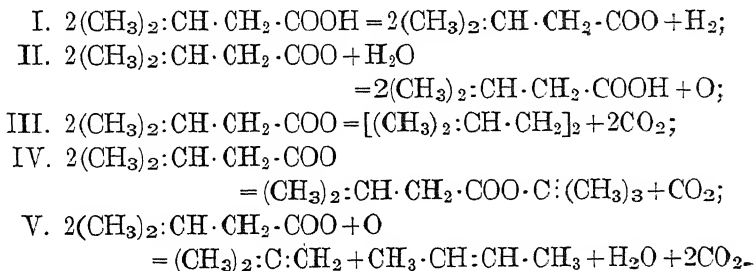
<sup>4</sup> Ztschr. f. phys. Chem. **33**, 295 (1900).

the evolved gases butylene and also hydrogen and oxygen were found. A small quantity of butyl alcohol, which was further oxidized to butyric aldehyde, was also formed by the saponification of butyl valerate.

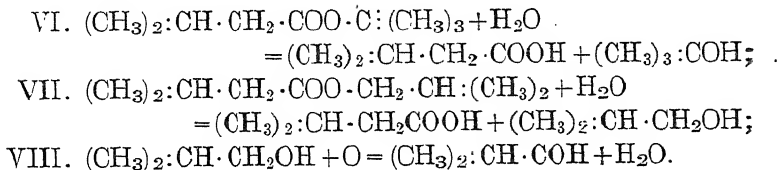
The oil which is formed in the electrolysis of potassium isovalerate is composed of diisobutyl and trimethylmethyl isovalerate, besides a small quantity of isobutyl isovalerate and isobutyric aldehyde. By saponification of the ester, trimethylcarbinol accompanied by a trifling quantity of isobutyl alcohol is found in the solution.

$\beta$ -butylene and isobutylene could be detected in the evolved gases.

Petersen adduces the following equations of reactions as the predominating ones:



To the above may be added the following equations of minor importance:



Even this complicated scheme cannot claim to be complete. Probably some entirely different reactions which have thus far not been elucidated, occur also. Considerable differences between the yields theoretically expected and those actually obtained point to such a supposition.

**Trimethylacetic Acid** (*Pivalic acid*)—the third of the valeric acids—has also been investigated by Petersen. It yields trimethylcarbinol and probably hexamethylethane, besides an isomeric body, and also two isomeric butylenes, isobutylene predominating with perhaps also  $\beta$ -butylene. Aldehyde is not formed; neither is an ester formed.

The principal processes taking place are the following:

- I.  $2\text{C}(\text{CH}_3)_3\text{COOH} = 2\text{C}(\text{CH}_3)_3\text{COO} + \text{H}_2$ ;
- II.  $2\text{C}(\text{CH}_3)_3\text{COO} + \text{H}_2\text{O} = 2\text{C}(\text{CH}_3)_3\text{COOH} + \text{O}$ ;
- III.  $2\text{C}(\text{CH}_3)_3\text{COO} = \text{C}(\text{CH}_3)_3 \cdot \text{C}(\text{CH}_3)_3 + 2\text{CO}_2$ ;
- IV.  $2\text{C}(\text{CH}_3)_3\text{COO} + \text{O} = 2(\text{CH}_3)_2\text{C}:\text{CH}_2 + \text{H}_2\text{O} + 2\text{CO}_2$ .

The trimethylcarbinol, a secondary product, is probably formed<sup>1</sup> by the addition of water to the isobutylene.

The electrolysis of these three isomeric acids affords thus considerable qualitative differences in the results. Summing up the whole matter, it can be said that the electrolysis of a valeric acid gives octane, butyl valerate, butylene, butyl alcohol, and butyric aldehyde.

1. The normal valeric acid yields normal compounds exclusively.

2. Isovaleric acid gives diisobutane, trimethylmethyl isovalerate, and trimethylcarbinol, also a little isobutyl isovalerate, isobutyl alcohol, and isobutyric aldehyde, and, finally, two isomeric butylenes, isobutylene and  $\beta$ -butylene.

The products resulting from the electrolysis of trimethylacetic acid have been summarized above.

The fourth isomeric valeric acid (active), *ethylmethylacetic acid*, has not yet been investigated.

**n-Caproic Acid.**—A concentrated solution of the potassium salt gave decane, and traces of the amyl ester of caproic acid, both of which are normal decomposition products. The electrolyses were made by Brazier and Gossleth,<sup>2</sup> and by Wurtz.<sup>3</sup>

<sup>1</sup> Ztschr. f. phys. Chemie **33**, 716 (1900).

<sup>2</sup> Lieb. Ann. **75**, 265 (1850).

<sup>3</sup> Ann. chim. phys. [3] **44**, 291 (1855).

The electrolytic relations in the decomposition of caproic acid were investigated by Rohland,<sup>1</sup> who electrolyzed the alkali salt. He obtained normal decane,  $C_{10}H_{22}$ .

Petersen<sup>2</sup> investigated the electrolysis of potassium caproate on a larger scale. The oil which separated during the passage of the current consisted of normal decane, a little amyl caproate and amyl alcohol, a trifling quantity of amylene, and an aldehyde, probably  $CH_3(CH_2)_3COH$ . The greater quantity of the amylenes formed during the electrolysis was found in the gaseous mixture; isopropylethylene,  $(CH_3)_2CHCH:CH_2$ , was probably present with the normal amylene,  $CH_3CH_2CH_2CH:CH_2$ .

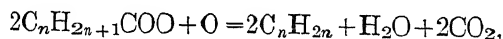
**n-Heptylic Acid, Oenanthylic Acid.**—The normal acid was electrolyzed by Brazier and Gossleth,<sup>3</sup> under conditions similar to those for caproic acid, and gave two hydrocarbons,  $C_{12}H_{26}$  and  $C_{12}H_{24}$ , in addition to hydrogen, potassium carbonate, and acid potassium carbonate.

On electrolyzing a concentrated solution of potassium n-heptylate, Rohland<sup>4</sup> obtained, besides dodecane,  $C_{12}H_{26}$ , a small quantity of a mixture of unsaturated hydrocarbons of the series  $C_nH_{2n}$  boiling at  $145^\circ$ .

**n-Caprylic Acid.**—Rohland<sup>5</sup> electrolyzed a concentrated potassium-salt solution of this acid and obtained the hydrocarbon tetradecane,  $C_{14}H_{30}$ .

**Pelargonic Acid**, under similar conditions, gives the hydrocarbon dioctyl.

The formation of olefines, in the electrolysis of aliphatic monocarboxylic acids, depends, perhaps, not upon an oxidation process,



<sup>1</sup> Ztschr. f. Elektrochemie 4, 120 (1897).

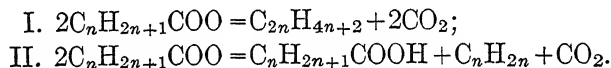
<sup>2</sup> Ztschr. f. phys. Chem. 33, 317 (1900).

<sup>3</sup> Lieb. Ann. 75, 265 (1850).

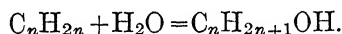
<sup>4</sup> Ztschr. f. Elektrochemie 4, 120 (1897).

<sup>5</sup> l. c.

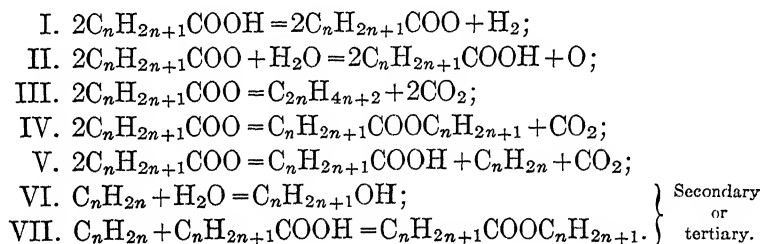
but upon a mutual reaction of the anions, analogously to that which causes the formation of saturated hydrocarbons:



The occurrence of secondary or tertiary alcohols depends presumably upon the addition of water to the olefines:



According to Petersen,<sup>1</sup> the equations expressing the general decomposition of aliphatic acids are the following:



Of the unsaturated monocarboxylic acids, *undecylenic acid* and *oleic acid* have been investigated by Rohland.<sup>2</sup> Both yielded, on electrolyzing their potassium salts in aqueous solution, a mixture of unsaturated hydrocarbons, the nature of which was not determined.

**Electrolysis of Mixtures.**—Wurtz<sup>3</sup> was the first to conceive the extremely fruitful idea in electrosynthesis of making syntheses of substances with mixed radicals by electrolyzing two components. After discovering his hydrocarbon synthesis, which depends upon the action of sodium upon alkyl iodides, and the use of the method in the preparation of "mixed radicals" from two different alkyl iodides, he also tried to obtain

<sup>1</sup> Ztschr. f. phys. Chem. **33**, 720 (1900).

<sup>2</sup> l. c.

<sup>3</sup> Ann. chim. phys. [3] **44**, 275 (1855); Jahresb. f. Chem. 1855, 575.

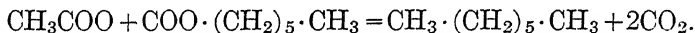


mixed hydrocarbons by electrolyzing the salts of fatty acids, using Kolbe's hydrocarbon synthesis:

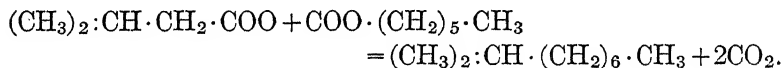


The successful results of these experiments prompted various investigators to select, as the materials for the starting-point of their electrolysis, mixtures of substances whose electrolytic intermediate products could mutually react. v. Miller and Hofer made use of these forms of reactions in the fatty-acid series for accomplishing the syntheses of acids. Löb in a similar manner prepared mixed azo-compounds in the aromatic series. The following are the experiments made by Wurtz:

*Potassium acetate* and *potassium ænanthylate* yield trifling quantities of heptane (methylcaproyl, Wurtz):



*Potassium valerate* and *potassium ænanthylate* give the expected mixed hydrocarbon, a decane, as chief product (butylcaproyl, Wurtz):



There are formed also a little octane, dodecane, and unsaturated hydrocarbons.

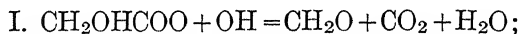
In the following discussion the description of the electrolysis of mixtures is given under the heading of the highest hydrocarbon component, since the reaction in electrolysis depends upon the nature of the components of the mixtures; thus the behavior of each separate component will then have been previously described.

## II. Monobasic Alcohol- and Ketonic Acids.

### a. Alcohol- (Hydroxy-) Acids.

While the acid anions of the unsubstituted aliphatic monocarboxylic acids react preponderatingly by splitting off carbonic

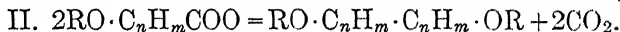
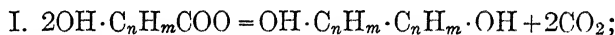
acid, without further oxidation of the radical united to the carboxyl group, the anion of the hydroxy-acids is regularly oxidized further. The extent of the oxidizing action depends, among other circumstances, to a great extent upon the concentration. For example, glycollic acid in concentrated solutions is oxidized almost completely to formaldehyde, and to a less extent to formic acid and carbonic acid. By increasing the dilution carbon monoxide occurs in place of formaldehyde.<sup>1</sup>



The substitution of methyl for hydroxyl does not affect the easy oxidability. It is evident from the theoretical explanations given in the first chapter that the changes in concentration are of importance for the course of the reaction only in so far as they influence the anode potential. By artificially keeping the latter constant, the products must remain the same, being independent of the conditions of concentration. In general, the following rules can be adduced for the electrolysis of oxy-acids (chiefly worked out by Miller and Hofer,<sup>2</sup> and Hamonet<sup>3</sup>):

$\alpha$ -Oxy-acids are converted by electrolysis in concentrated solution into aldehydes or ketones. If the solution is more highly diluted, the compound is oxidized to carbon monoxide.

$\beta$ -Oxy-acids behave more like acetic acid; they are, at least partially, converted into glycols, or their ethers:



In the case of dioxy-acids the oxidation affects both hydroxyl groups, the intermediate  $\text{CHOH}$ -groups being oxidized to carbon mon- or dioxide.

<sup>1</sup> Ber. d. deutsch. chem. Gesellsch. **27**, 461 (1894).

<sup>2</sup> Ibid.

<sup>3</sup> Compt. rend. **132**, 259 (1901).

The experiments of Miller and Hofer were made by passing the electrolyte in a slow stream through the cell (Apparatus, Fig. 4, p. 44). This made it possible to find decomposition products which would otherwise have been changed by further electrolysis; a more complete expression of the course of the decomposition was thus obtained. It is to be regretted that the researches do not mention the necessary data regarding the electrical conditions.

**Glycollic Acid.**—If a solution of 30 g. sodium glycollate in 38 cc. water is electrolyzed with a current strength of 1 amp., there are formed chiefly carbonic acid and formaldehyde, besides a little carbon monoxide, formic acid, and oxygen (Miller and Hofer<sup>1</sup>). Walker<sup>2</sup> obtained aldehyde in the electrolysis of the sodium salt of *ethyl glycollic ether*.

**Methoxyglycollic Acid.**—The electrolysis of its sodium salt was made by the same authors<sup>3</sup> and yielded formaldehyde, methylal, formic acid, and carbonic acid; in dilute solution also carbon monoxide and a little methyl alcohol.

A mixture of potassium glycollate and potassium acetate unites at the positive pole to form ethyl alcohol (Miller and Hofer<sup>4</sup>); some acetaldehyde is also formed by further oxidation:



#### Oxypropionic Acids.

**Ordinary Lactic Acid.**—As Kolbe<sup>5</sup> had already discovered, the concentrated solution of the potassium salt gave carbon dioxide and acetic aldehyde. The investigators above mentioned also observed the presence of some formic acid. When the solution surrounding the positive pole was kept slightly

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<sup>1</sup> Ber. d. deutsch. chem. Gesellsch. **27**, 467 (1894).

<sup>2</sup> Journ. Chem. Soc. **65**, 1278 (1896).

<sup>3</sup> Ber. d. deutsch. chem. Gesellsch. **27**, 469 (1894).

<sup>4</sup> Ibid. **28**, 2437 (1895).

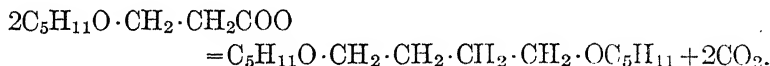
<sup>5</sup> Lieb. Ann. **113**, 214 (1860).

alkaline, aldol and crotonic aldehyde were formed instead of acetic aldehyde.

**Sarcosolactic Acid.**—When the solution surrounding the positive pole was kept neutral, a concentrated solution of the sodium salt yielded acetic aldehyde and carbon dioxide.

**Hydracrylic Acid** (Ethylenelactic Acid =  $\beta$ -oxypropionic Acid).—Resin and a little formic acid were found present in the electrolyte surrounding the positive pole.

The potassium salt of the alcoholic amyl ether of this acid, the  $\beta$ -amyloxypropionic acid, was electrolyzed by Hamonet.<sup>1</sup> It gave about 50 per cent of the theoretical yield of 1.4-butanedioldiamyl ether (diamyl ether of butylene glycol).



**Glyceric Acid** (Dioxypropionic Acid).—This acid decomposes into carbon mon- and dioxide, formaldehyde, and formic acid (Miller and Hofer).

#### Oxybutyric Acids.

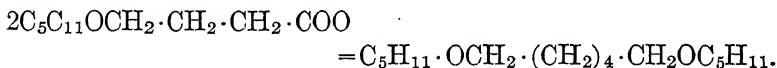
**$\alpha$ -Oxybutyric Acid** ( $CH_3 \cdot CH_2 \cdot CHOH \cdot COOH$ ).—This substance was converted into carbon dioxide, propionic aldehyde, and some formic acid (Miller and Hofer).

**$\alpha$ -Oxyisobutyric Acid** ( $(CH_3)_2 : CHOH - COOH$ ).—This compound, investigated in the same manner, was found to be partially oxidized at the anode to acetone. Much carbonic acid and a little carbon monoxide is also evolved.

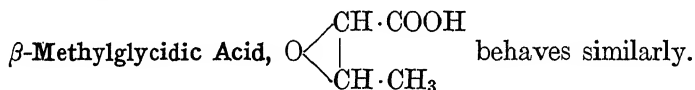
**$\beta$ -Oxybutyric Acid** ( $CH_3 \cdot CH(OH) \cdot CH_2 \cdot COOH$ ).—From this acid were obtained in the positive electrolyte crotonic aldehyde and a little formic acid, also resinous substances. Considerable quantities of carbonic acid, also a little carbon monoxide and unsaturated hydrocarbons, are formed. The small quantities

of saturated hydrocarbons are derived probably from impurities in the acid (presence of acetic acid).

**$\gamma$ -Oxybutyric Acid** ( $\text{CH}_2\text{OH} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{COOH}$ ).—Hamonet<sup>1</sup> electrolyzed the alkali salt of  $\gamma$ -isoamyloxybutyric acid in order to obtain symmetrical hexylene glycol, or its diamyl ether. The desired reaction did not take place:



**$\beta$ -Methylglyceric Acid** ( $\alpha$ - $\beta$ -Dioxybutyric Acid (M. Pt. 74–75°) =  $\text{CH}_3 \cdot \text{CHOH} \cdot \text{CHOH} \cdot \text{COOH}$ ).—When the potassium salt of this acid is electrolyzed (Pissarszewski<sup>2</sup>) it breaks up into carbon mon- and dioxide, formaldehyde, formic acid, acetaldehyde, acetic acid, and another substance having the property of reducing Fehling's solution. This latter compound was not isolated.



### b. Ketonic Acids.

Pyroracemic and lævulinic acid, i.e., an  $\alpha$ - and a  $\gamma$ -ketonic acid are the only monobasic ketonic acids which have been electrolyzed. The electrolysis of a representative of a  $\beta$ -ketonic acid, acetoacetic acid, could not be carried out, on account of the instability of the free acid and its salts. The reactions take place partly in a manner similar to those occurring in the decomposition of acetic acid; the anions unite to form a diketone, carbonic acid being split off; and partly in a further oxidation to acetic acid, with the occurrence of carbon mon- and dioxides.

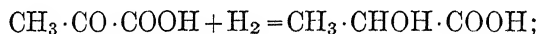
<sup>1</sup> Compt. rend. **136**, 96 (1903).

<sup>2</sup> Ztschr. d. russ. chem. phys. Gesellsch. **29**, 289, 338 (1897).

**Pyroracemic Acid.**—Potassium pyroracemate gives (Hofer)<sup>1</sup> chiefly acetic acid and also a little diacetyl:

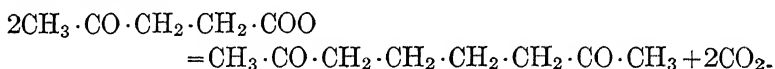


Rockwell<sup>2</sup> found at the anode some acetaldehyde, and at the cathode the normal reduction product of pyroracemic acid, i.e.  $\alpha$ -lactic acid:



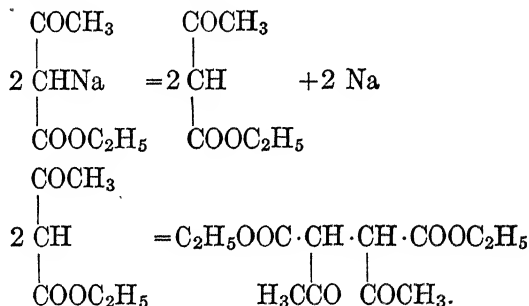
also some propionic acid, probably formed by further reduction.

**Lævulinic Acid.**—This acid is much better adapted for the synthesis of the corresponding diketone than is pyroracemic acid. Hofer,<sup>3</sup> on electrolyzing the potassium salt of the acid, obtained about 50% of the theoretically expected quantity of 2,7-octandion:



Considerable quantities of acetic acid are also formed, and some carbon monoxide is produced by the oxidation of the methylene groups.

**Acetoacetic Acid.**—If the sodium compound of acetoacetic ester (Weems<sup>4</sup>) in alcoholic solution is electrolyzed, there is formed diacetylsuccinic ester:



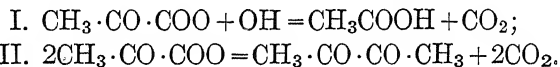
<sup>1</sup> Ber. d. deutsch. chem. Gesellsch. **33**, 650 (1900).

<sup>2</sup> Journ. Amer. Chem. Soc. **24**, 719 (1902).

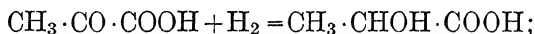
<sup>3</sup> l. c.

Amer. Chem. Journ. **16**, 569 (1894).

**Pyroracemic Acid.**—Potassium pyrорacemate gives (Hofer)<sup>1</sup> chiefly acetic acid and also a little diacetyl:

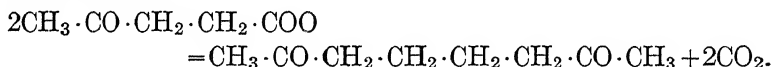


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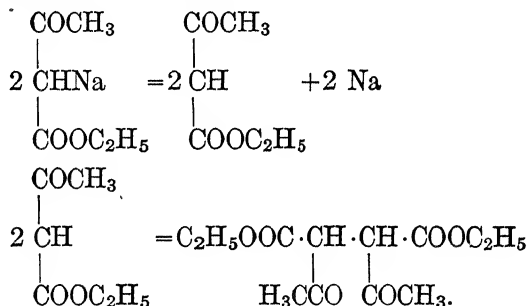
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<sup>1</sup> Ber. d. deutsch. chem. Gesellsch. **33**, 650 (1900).

<sup>2</sup> Journ. Amer. Chem. Soc. **24**, 719 (1902).

<sup>3</sup> l. c.

Amer. Chem. Journ. **16**, 569 (1894).

According to Tafel and Friedrichs,<sup>1</sup> acetoacetic ester can be easily reduced in sulphuric-acid solution. This reduction evidently extends to the carbox-ethyl group because a molecule of the ester requires almost six atoms of hydrogen.

*Acetylmalonic Acid*,  $\text{CH}_3 \cdot \text{CO} \cdot \text{CH} : (\text{COOH})_2$ , and *Acetone-dicarboxylic Acid*,  $\text{CO} : (\text{CH}_2\text{COOH})_2$ , do not permit their anions to unite (Weems<sup>2</sup>).

In connection with his investigation of ketonic acids, Hofer<sup>3</sup> has used the electrosynthetic reaction, previously discovered with Miller,<sup>4</sup> which consists in electrolyzing potassium salts of organic acids in mixture with potassium acetate and other lower fatty acids. The general nature of the reaction is that the two anions unite, as in Kolbe's synthesis, carbonic acid being split off, e.g.,

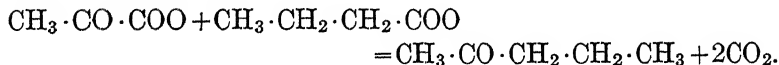


*Potassium Pyroracemate* and *Potassium Acetate* thus yield acetone as the chief product:



Some acetic methyl ester and traces of diacetyl are also formed.

*Potassium Pyroracemate* and *Potassium Butyrate* unite to form methylpropylketone:



Some diacetyl is also formed in this case, with trifling quantities of esters of butyric acid, and larger quantities of hydrocarbons, chiefly hexane and decane. The hexane was formed from the butyric acid, the decane from caproic acid, an impurity in the butyric acid.

<sup>1</sup> Ber. d. deutsch. chem. Gesellsch. **37**, 3188 (1904).

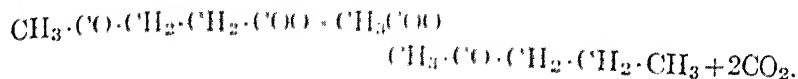
<sup>2</sup> l. c.

<sup>3</sup> Ber. d. deutsch. chem. Gesellsch. **33**, 650 (1900).

<sup>4</sup> Ibid. **28**, 2427 (1895).

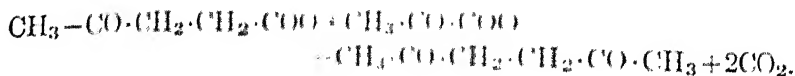


*Potassium Lactinate* and *Potassium Acetate* yield, analogously, methylpropylketone:



At the same time a larger quantity of 2,7-octandion could be isolated.

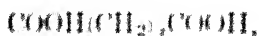
*Potassium Lactinate* and *Potassium Pyruvate* unite to form the expected acetylacetone, besides a little 2,7-octandion:



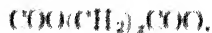
### III. Dibasic Acids.

Most beautiful results of the application of electrolytic decompositions in a direct synthesis have been accomplished with dibasic acids. The results have a practical as well as a theoretical value,—as useful methods of preparing compounds for the laboratory, and as proofs for certain constitutions. The researches of Brown and Walker<sup>1</sup> have opened up an extremely fruitful domain.

The dibasic acids having the constitution



when electrolyzed as such or as their soluble salts, discharge at the anode the anions

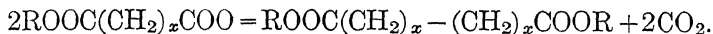


These give hydrocarbons, mostly unsaturated and in poor yield, carbonic acid being split off. The reaction observed in the case of acetates does not here predominate.

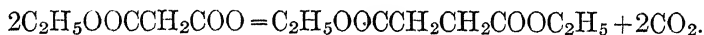
Simple and smooth reactions, however, are obtained if an ester group is introduced into the dibasic fatty acids. Since

<sup>1</sup> Lieb. Ann. 261, 107 (1891); 274, 41 (1893).

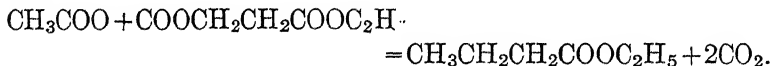
ester groups, according to an experiment of Guthrie,<sup>1</sup> are electrolytically inactive, the mono-esters of dibasic acids behave like monobasic acids, i.e. carbon dioxide is split off and diesters of higher dibasic acids are formed, saponification converting the esters into the free dibasic acids:



Thus the diethyl ester of succinic acid is formed from ethyl potassium malonate:



Von Miller and Hofer<sup>2</sup> broadened the possibility of the electro-syntheses of dibasic acids by borrowing an idea of Wurtz and using the results of Brown and Walker. Wurtz,<sup>3</sup> as already mentioned, had electrolyzed mixtures of two fatty-acid salts, and accomplished the union of the different radicals to form the corresponding hydrocarbons. In the same manner, von Miller and Hofer electrolyzed mixtures of fatty-acid salts and mono-esters of dicarboxylic acids. Hereby the esters of monocarboxylic acids containing a higher number of carbon atoms are formed. If, for instance, a mixture of potassium acetate and potassium ethyl succinate is subjected to electrolysis, butyric ethyl ester is formed, according to the following equation:



If the two carboxyl groups of dibasic acids are esterified, such a di ester can behave as an acid only when methylene groups possessing a decidedly acid character are present. Mulliken<sup>4</sup> and Weems<sup>5</sup> investigated such compounds. The sodium

<sup>1</sup> Lieb. Ann. **99**, 65, 1856.

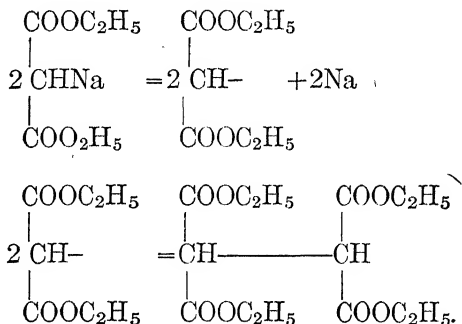
<sup>2</sup> Ber. d. deutsch. chem. Gesellsch. **28**, 2427 (1895).

<sup>3</sup> Jahresber. d. Chem. 575 (1855).

<sup>4</sup> Amer. Chem. Journ. **15**, 323 (1893).

<sup>5</sup> Ibid **16**, 569 (1894).

compounds of diethyl esters of dibasic acids in particular frequently behave in a manner analogous to that of the carboxylic acids, the anions uniting. The same compounds are thus obtained as are formed by the elimination of sodium by iodine. Thus sodium diethylmalonic ester gives ethanetetracarboxylic ester:



If the methylene groups of dicarboxylic acids contain electrolytically sensitive radicals, the reaction picture is shifted, as will be touched upon in the special cases.

**Oxalic Acid.**—The deportment of the saturated solution of the free acid on electrolysis was determined by Brester,<sup>1</sup> Bourgoin,<sup>2</sup> Balbiano and Alessi,<sup>3</sup> Bunge,<sup>4</sup> and Renard.<sup>5</sup> The general result was that oxygen and carbon dioxide were obtained at the anode and hydrogen at the cathode. It is possible to completely oxidize oxalic acid to carbon dioxide. On this property depends the great importance of oxalic acid in quantitative electrolytic analysis, into which it has been introduced by Classen.<sup>6</sup>

The ability of ammonium oxalate to form soluble double salts with many difficultly soluble or insoluble metallic salts is in accord with the favorable conduct of the acid on electroly-

<sup>1</sup> Jahresb. f. Chem. 87 (1866).

<sup>2</sup> Compt. rend. 67, 97 (1868).

<sup>3</sup> Gazz. chim. 12, 190 (1882); Ber. d. deutsch. chem. Gesellsch. 15, 2236 (1882).

<sup>4</sup> Ber. d. deutsch. chem. Gesellsch. 9, 78 (1876).

<sup>5</sup> Ann. chim. phys. [5] 17, 289 (1878).

<sup>6</sup> Classen, Quan. Analysis by Electrolysis (Wiley & Sons, N. Y.).

sis, by which operation it may be entirely removed from the solution in the form of gas.

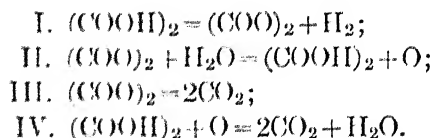
The reducing effects of the current on oxalic acid were also observed. Thus on electrolyzing both the free acid and its sodium salt Barbiano and Alessi were able to prove the presence of glycollic acid. Tafel and Friedrichs<sup>1</sup> obtained a good yield of glyoxylic acid by reducing oxalic acid in sulphuric-acid solution at lead or mercury cathodes. Oxalic ester and oxal-acetic ester are easily reduced also.

The oxidation is not complete if the electrolysis is conducted in the cold solution, carbon monoxide as well as carbon dioxide being then formed at the positive pole.

The decomposition reactions of oxalates are entirely analogous to those of the free acid. In alkaline solution the oxidation proceeds more rapidly than in neutral solution because of the better conductivity of the alkalies.

Naturally ethyl potassium oxalate cannot react in accordance with the scheme of the Brown and Walker's syntheses. When it was electrolyzed both investigators<sup>2</sup> observed the presence of ethylene. This unsaturated hydrocarbon was very likely derived from the ester group.

Petersen<sup>3</sup> has formulated the following equations of decomposition:



These data on the electrolysis of oxalic acid must be supplemented by those regarding its reduction to glycollic acid, glyoxylic acid, and the reduction to formic acid (Royer<sup>4</sup>),

<sup>1</sup> Ber. d. deutsch. chem. Gesellsch. **37**, 3189 (1904).

<sup>2</sup> Lieb. Ann. **274**, 70 (1893).

<sup>3</sup> Ztschr. f. phys. Chem. **33**, 698 (1900).

<sup>4</sup> Compt. rend. **69**, 1374 (1869), **70**, 731 (1870).

which is brought about when using oxalic acid in place of nitric acid in a Grove cell.

A series of researches concerning the relation between the oxidation of oxalic acid and the electrical conditions have been made. Oettel<sup>1</sup> discovered that the current consumption required for an oxidation process is greater when a smaller current density is used than when a higher density is employed. Åckerberg<sup>2</sup> determined that the oxidation, which is trifling at a polished platinum anode, is quantitative under the same conditions at a platinized anode. Salzer<sup>3</sup> investigated the electrolysis of oxalic acid, as to the tension conditions and oxidation action, in sulphuric-acid and in aqueous solutions at polished (bright) and platinized anodes.

**Malonic Acid.**—This acid was investigated by Bourgoin.<sup>4</sup> In a concentrated solution of sirupy consistency it, like oxalic acid, is only slowly oxidized to carbon dioxide, with evolution of oxygen. A strongly concentrated solution of the unaltered acid is found surrounding the positive electrode, even after an electrolysis of long duration. On electrolysis of the sodium salt carbon monoxide is also present in the gaseous mixture evolved. The proportions of the various gases, carbon monoxide and dioxide, and oxygen, remain fairly constant during the period of electrolysis (85.8%, 9.7%, 4.5%).

In alkaline solution the decomposition products are the same as in neutral solution, only the proportions of the individual gases being different, and varying according to the duration of the electrolysis.

Miller,<sup>5</sup> on electrolyzing malonates, was able to detect a trifling quantity of ethylene.

Petersen<sup>6</sup> verified this fact. He formulated the following reactions:

<sup>1</sup> Ztschr. f. Elektrochemie 1, 90 (1894).

<sup>2</sup> Ztschr. f. anorg. Chem. 31, 161 (1902).

<sup>3</sup> Ztschr. f. Elektrochemie 8, 897 (1902).

<sup>4</sup> Ann. chim. phys. [1] 14, 157 (1857); Bull. d. l. soc. chim. 33, 417 (1889).

<sup>5</sup> Journ. f. prakt. Chemie 127, 328 (1879).

<sup>6</sup> Ztschr. f. phys. Chemie 33, 700 (1900).

- I.  $\text{CH}_2(\text{COOH})_2 = \text{CH}_2(\text{COO})_2 + \text{H}_2$ ;  
 II.  $\text{CH}_2(\text{COO})_2 + \text{H}_2\text{O} = \text{CH}(\text{COOH})_2 + \text{O}$ ;  
 III.  $2\text{CH}_2(\text{COO})_2 = \text{C}_2\text{H}_4 + 4\text{CO}_2$ ;  
 IV.  $\text{CH}_2(\text{COO})_2 + \text{O}_2 = \text{CO} + \text{H}_2\text{O} + 2\text{CO}_2$ ;

in which, however, III is inconsiderable.

The Brown-Walker<sup>1</sup> method has been found to be of excellent service in the electrolysis of the potassium salts of the mono-esters of malonic acid. The formation of the diethyl ester of succinic acid from ethyl potassium malonate has already been mentioned (p. 103).

If the ethyl potassium salts of substituted acids are chosen as the starting-point, it is possible to obtain disubstituted acids, according to the above reactions.

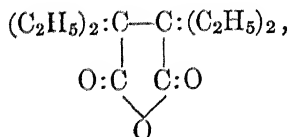
1. *Ethyl potassium methylmalonate* yields the two symmetrical dimethylsuccinic acids having the melting-points  $193^\circ$  and  $121^\circ$ .

2. *Ethyl potassium ethylmalonate* yields the corresponding symmetrical diethylsuccinic acids, with the melting-points  $192^\circ$  and  $130^\circ$ .

3. *Ethyl potassium dimethylmalonate* affords *tetramethylsuccinic acid*.

4. From *ethyl potassium diethylmalonate* a substance having the composition  $\text{C}_{14}\text{H}_{26}\text{O}_4$ , and which differs from the expected tetraethylsuccinic acid by  $\text{C}_2\text{H}_4$ , was obtained. The nature of this body has not yet been determined.

Hydrobromic acid splits off alcohol, the compound  $\text{C}_{12}\text{H}_{20}\text{O}_3$ , which has perhaps the furfurane formula

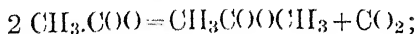


being formed.

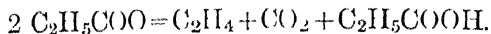
All these reactions do not take place smoothly, but are accompanied by secondary reactions, principally oxidations,

<sup>1</sup>l. c.

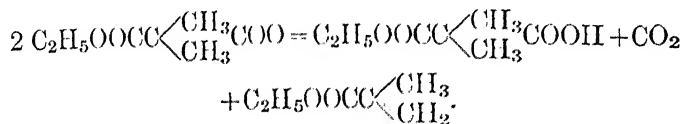
which are limited as much as possible by working with strong concentrated solutions and low temperatures. Moreover, the formation of esters also is always possible according to the equation



and, finally, the formation of unsaturated esters may take place analogously to the formation of ethylene from propionic acid:



Thus it was possible to isolate *methylacrylic acid* by the electrolysis of *ethyl potassium dimethylmalonate*:



In the same way *ethylcrotonic acid* is formed from the *ethyl potassium salt of diethylmalonic acid*.

Mulliken,<sup>1</sup> on electrolyzing *sodium malonic diethyl ester* in alcoholic solution, obtained *ethanetetra-carboxylic ester*, as already mentioned. Weems,<sup>2</sup> on electrolyzing the corresponding compound of *methylmalonic acid*, obtained *dimethylethanetetra-carboxylic ester*, whereas *ethylmalonic ester* gave *diethylethanetetra-carboxylic ester*.

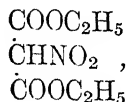
The method of von Miller,<sup>3</sup> electrolyzing *potassium ethylmalonate* with *potassium salts of aliphatic carboxylic acids*, also gives satisfactory results. If *potassium acetate* is chosen as the second component of the electrolytic mixture, propionic ethyl ester is formed; and likewise by using *potassium propionate* or *potassium butyrate* we obtain butyric ethyl ester or valeric ethyl ester respectively.

<sup>1</sup> Amer. Chem. Journ. **15**, 323 (1893).

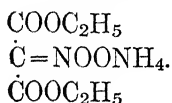
<sup>2</sup> Ibid. **16**, 569 (1894).

<sup>3</sup> Ber. d. deutsch. chem. Gesellsch. **28**, 3438 (1895).

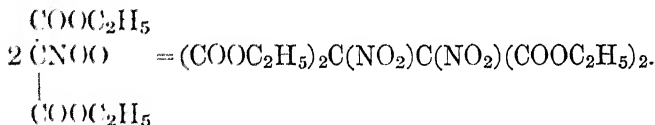
**Nitromalonic Acid.**—According to Ulpiani and Gasparini,<sup>1</sup> a hydro-alcoholic solution of nitromalonic ethyl ester does not conduct the current, but an aqueous solution of the ammonium salt does. According to this the ester appears as a true nitro-compound:



but its ammonium salt, on the contrary, as an isnitro-salt:



The electrolysis of this latter does not give the free isonitro acid at the anode, but the *dinitroethanetetracarboxylic ester*:



The ammonium salt of *nitromalonamide* yields at the anode, only free nitromalonamide, whereas *fulminuric acid* (nitrocyanacetamide),  $\text{CN} \cdot \text{CH}(\text{NO}_2) \cdot \text{C} \begin{smallmatrix} \text{OH} \\ \diagup \\ \text{NH} \end{smallmatrix}$ , on electrolysis of its ammonium salt, gives a new reaction product which has not yet been investigated.

**Succinic Acid.**—Bourgoin<sup>2</sup> and Kekulé<sup>3</sup> found that the free acid underwent oxidation with difficulty, only a small quantity of carbon monoxide in addition to some oxygen and carbon dioxide being formed.

The neutral sodium salt gave the same products, as did also the alkaline solution of this salt, except that in the latter experiment the formation of carbon monoxide predominated. If, however, four molecular equivalents of sodium succinate were

<sup>1</sup> Gazz. chim. **32**, II, 235 (1902); Ztschr. f. Elektrochemie **9**, 477 (1903).

<sup>2</sup> Ann. de chim. et phys. (4) **14**, 157 (1866).

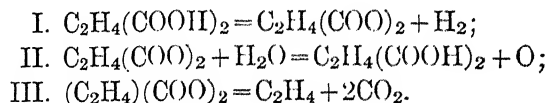
<sup>3</sup> Lieb. Ann. **131**, 84 (1864).



treated with one equivalent of sodium hydroxide, ethylene and a little acetylene could also be detected. Kolbe<sup>1</sup> states that methyl oxide is also formed; Bourgoin, however, was unable to confirm this statement.

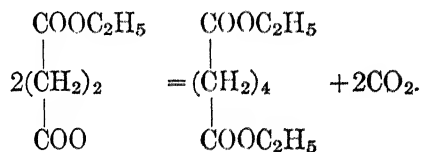
Clarke and Smith,<sup>2</sup> on oxidizing succinic acid in alkaline solution, obtained, besides oxygen, carbon mon- and dioxide, ethylene, methane, tartaric acid, and oxalic acid.

Petersen<sup>3</sup> was unable to detect either carbon monoxide or acetylene in a slightly acid electrolytic solution of potassium succinate. The following equations essentially express the course of the electrolysis:

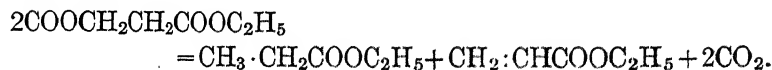


Small variations in the conditions of the experiment, as well as in the degree of acidity, the temperature, and the kind and size of the electrodes, exert a great influence on the course of the electrolysis.

According to the method of Brown and Walker,<sup>4</sup> adipic diethyl ester is formed from ethyl potassium succinate:



Fairly large quantities of propionic and acrylic esters are also formed, probably by the reaction



<sup>1</sup> Lieb. Ann. **113**, 244 (1860).

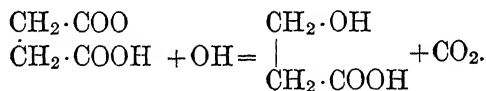
<sup>2</sup> Journ. Amer. Chem. Soc. **21**, 967 (1899).

<sup>3</sup> Ztschr. f. physik. Chem. **33**, 701 (1900).

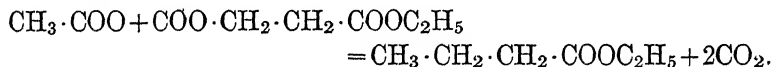
<sup>4</sup> l. c.

Bouveault<sup>1</sup> claims that the yield of adipic acid is better on electrolyzing the methyl ester-salt in methyl-alcoholic solution. He obtained a yield of 80% by using a mercury cathode and a hollow platinum spiral anode, through which a current of cold water was passed. The acid succinic methyl ester occurs as the principal by-product, also a neutral methyl ester of a tribasic acid which was not investigated.

Sodium succinate and sodium perchlorate, electrolyzed by Hofer and Moest,<sup>2</sup> gave hydracrylic acid as the chief product, besides acetaldehyde, acetic acid, methyl alcohol, and formic acid. The splitting off of carbonic acid and the introduction of the hydroxyl group occurs only at one carboxyl group:

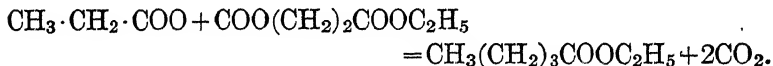


Von Miller and Hofer<sup>3</sup> have also carried out the principle of the electrolysis of mixtures, discussed under malonic acid, using potassium ethyl succinate, and submitting the latter to electrolysis at the anode with potassium salts of monocarboxylic acids. They thus obtained on the addition of *potassium acetate* about 69% of the theoretical quantity of butyric ethyl ester:



Incidentally a yield of about 22% of adipic ester was obtained.

The synthesis of valeric ethyl ester from potassium ethyl succinate and *sodium propionate* was accomplished in the same way:

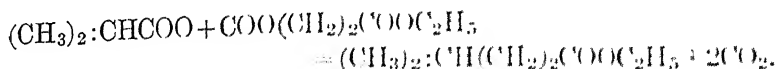


<sup>1</sup> Bull. soc. chim. **29**, 1038, 1043 (1903).

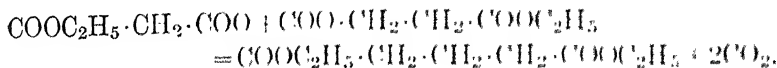
<sup>2</sup> Lieb. Ann. **323**, 284 (1902).

<sup>3</sup> Ber. d. deutsch. chem. Gesellsch. **28**, 2431 (1895).

Furthermore, by using a mixture of potassium ethyl succinate and *potassium isobutyrate*, isobutylic ester was obtained:



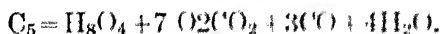
Vanzetti and Coppadoro<sup>1</sup> have extended the von Miller-Hofer method to the electrolysis of a mixture of *ethyl potassium malonate* and *ethyl potassium succinate*. They obtained a poor yield of the desired glutaric diethyl ester:



Moreover, succinic diethyl ester was formed from the malonic acid, and adipic diethyl ester from the succinic acid.

#### *Pyrotartaric Acid:*

**Glutaric Acid** (*Normal Pyrotartaric Acid*).—The results obtained by Reboul and Bourgoin<sup>2</sup> are the following: A large part of the acid remains unchanged, while a small part is decomposed according to the following equation:



A hydrocarbon of the composition  $\begin{array}{c} \text{CH}_2 \\ | \\ \text{CH}_2 \end{array} \text{CH}_2$  was not obtained; nor was an olefine formed.

Similar observations were made in the electrolysis of potassium glutarate, also in alkaline solution.

Petersen<sup>3</sup> expresses the course of the electrolysis by the following equations:

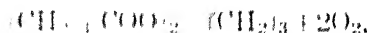
<sup>1</sup> Atti R. Accad. dei Lincei **12**, II, 209 (1903).

<sup>2</sup> Bull. soc. chim. **27**, 545 (1877); Compt. rend. **84**, 1231, 1395 (1877).

<sup>3</sup> Ztschr. f. phys. chem. **33**, 703 (1900).

- I.  $\text{CH}_2 + \text{COOH}_2 \rightarrow \text{CH}_2\text{CO}_2 + \text{H}_2$ ;
- II.  $\text{CH}_2 + \text{COO}_2 + \text{H}_2\text{O} \rightarrow (\text{CH}_2)_3(\text{COOH})_2 + \text{O}$ ;
- III.  $\text{CH}_2 + \text{COO}_2 + 3\text{O}_2 \rightarrow 2\text{CO}_2 + 3\text{CO} + 3\text{H}_2\text{O}$ .

The expected reaction,

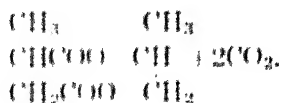


does not take place.

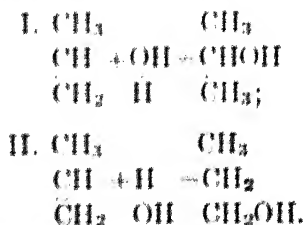
Brown and Walker<sup>1</sup> obtained the diethyl ester of suberic acid from ethyl potassium glutarate.

**Pyrotartaric Acid (Methylsuccinic Acid).** Reboul and Bourgoin, on electrolyzing a solution of the neutral potassium salt, obtained a deposit of the acid salt; the formation of such an acid salt in the case of glutaric acid does not occur. On continued electrolysis the crystals disappear, the free acid being regenerated. In alkaline solution, also, the formation of the acid salt occurs on prolonged electrolysis. Nevertheless the continuous, though slight, evolution of carbon dioxide and carbon monoxide is a proof of extensive oxidation.

Petersen,<sup>2</sup> on electrolyzing a 20% solution of potassium pyrotartrate, found propylene, besides carbon mon- and dioxide among the evolved gases:



Primary and secondary propyl alcohol could be isolated from the electrolyzed fluid, both of which seemed to be formed from propylene by addition of water:



<sup>1</sup>l. c.

<sup>2</sup>l. c.

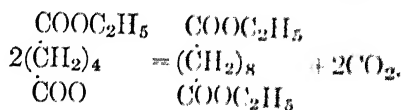
<sup>3</sup>l. c.

The strong aldehyde reaction of the electrolyte, after the experiment was finished, indicates that the primary alcohol is partially oxidized further to propionic aldehyde, or that the propylene can yield propylene oxide through the influence of the anodic oxygen, and, by molecular rearrangement, the aldehyde:

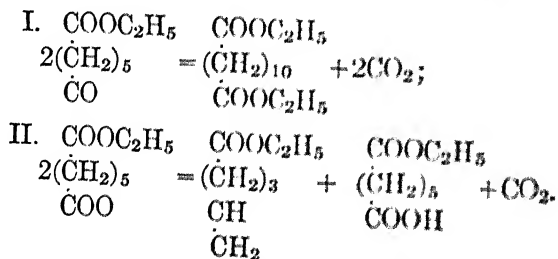


**Ethylmalonic Acid.**—The behavior of ethyl potassium ethylmalonate has already been mentioned in the discussion of malonic acid. The potassium salt, in a 20% slightly acid solution, yields propylene (Petersen<sup>1</sup>), and probably, like pyrotartaric acid, primary and secondary propyl alcohol.

**Adipic Acid.**—The ethyl potassium salt was converted into the sebacic diethyl ester by Brown and Walker<sup>1</sup>:



**Pimelic Acid.**—In the same manner, the diethyl ester of n-decanedicarboxylic acid is formed from the ester potassium salt of pimelic acid (Komppa,<sup>2</sup> also Walker and Lumsden<sup>3</sup>). n-Pentenecarboxylic ethyl ester occurs as a by-product at the anode:



<sup>1</sup> l. c.

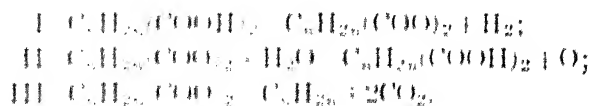
<sup>2</sup> Ber. d. deutsch. chem. Gesellsch. **34**, 900 (1901).

<sup>3</sup> Journ. Chem. Soc. **79**, 1197 (1901)

**Suberic Acid**, by the same method, gives the ester of *n*-decanedioic dibasic acid, likewise.

**Sebacic Acid**, the ester of *n*-decahexanedicarboxylic acid (octodecandi acid), besides sebacic diethyl ester and the ester of the unsaturated acid  $\text{CH}_2\text{CH}(\text{CH}_2)_8\text{COOH}$ .

The decompositions which the acids (or their potassium salts) of the cyclic acid series undergo can be essentially interpreted by the following equations:



#### IV. Unsaturated Dibasic Acids.

**Maleic Acid.** According to the investigations of Kekulé,<sup>1</sup> a concentrated solution of the sodium salt gives, on electrolysis, acetylene and also carbon dioxide at the anode, while a little sucrose acid is formed at the cathode. A molecular rearrangement to fumaric acid also occurs to a trifling extent. *Bromomaleic acid* decomposes into hydrobromic acid, and carbon monoxide and dioxide.

*Ethyl Potassium Maleate* does not react conformably to the reaction of Brown and Walker (Shields<sup>2</sup>), but gives, in concentrated solution, carbonic acid, oxygen, and unsaturated hydrocarbons; however, much of the material serving for the starting point remains unchanged.

**Fumaric Acid.** This acid was also investigated by Kekulé. At the beginning of the experiment it gives pure acetylene and carbon dioxide, but after the operation has continued for some time the acetylene was found to be mixed with oxygen. *Ethyl potassium fumarate* behaves exactly like the maleate.

**Itaconic Acid.** The concentrated solution of the alkali salt, electrolyzed by Aarland,<sup>3</sup> gave a hydrocarbon isomeric with allylene,  $\text{C}_3\text{H}_4$ , which is said to have the formula  $\text{CH}_2=\text{C}=\text{CH}_2$ ;

<sup>1</sup> *Lech. Ann.* **131**, 85 (1864).

<sup>2</sup> *Ibid.* **274**, 64 (1868).

<sup>3</sup> *Journ. prakt. Chem.* [2] **4**, 376 (1871), [2] **6**, 256 (1872).

along with this compound, some propylene was formed, while a portion of the acid was always regenerated.

**Citraconic Acid.**—The concentrated solution of the sodium salt, likewise electrolyzed by Aarland,<sup>1</sup> yielded, besides a hydrocarbon,  $C_3H_4$ , small traces of acrylic and mesaconic acid.

**Mesaconic Acid**, under similar conditions, gives the same hydrocarbon and traces of acrylic and itaconic acids.

The unsaturated acids, on electrolysis, consequently appear to give no synthetic products at all. The aromatic acids, like phthalic and benzylmalonic acid, behave similarly.

### V. Polybasic Acids.

**Malic Acid.**—The electrolysis of malic acid was effected by Bourgoin<sup>2</sup> and Brester.<sup>3</sup> Both the free acid, which is but slowly decomposed, and the neutral alkali salt, gave the same products, carbon dioxide and a little carbon monoxide and oxygen. After the completion of the experiment the solution contained some aldehyde and acetic acid. Von Miller and Hofer<sup>4</sup> also found crotonaldehyde.

**Tartaric Acid** (Dextro-rotary). The free acid is partially oxidized (Bourgoin<sup>5</sup> and Kekulé<sup>6</sup>) to carbon dioxide and carbon monoxide, while the solution contains acetic acid. Neutral potassium tartrate gives principally carbon dioxide besides a little carbon monoxide and oxygen, acid potassium tartrate being at the same time deposited. In alkaline solutions the same gases carry with them traces of ethane, the formation of which is due to potassium acetate, which is found present in the solution at the end of the operation; also some ethylene. Von Miller and Hofer<sup>7</sup> obtained from a concentrated solution of potassium tartrate carbon mon- and dioxides and oxygen,

<sup>1</sup> Journ. prakt. Chem. [2] 7, 142 (1873).

<sup>2</sup> Bull. soc. chim. [2] 9, 427 (1868).

<sup>3</sup> Ibid. 8, 23 (1867).

<sup>4</sup> Ber. d. deutsch. chem. Gesellsch. 27, 470 (1894).

<sup>5</sup> Compt. rend. 65, 1144 (1867); Bull. soc. chim. [2] 11, 405 (1869).

<sup>6</sup> Lieb. Ann. 131, 88 (1864).

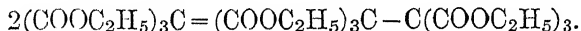
<sup>7</sup> Ber. d. deutsch. chem. Gesellsch. 27, 470 (1894).

with a little formaldehyde and formic acid, but no acetic acid and ethylene as affirmed by Bourgoin. The ethyl ester behaves in a like manner.

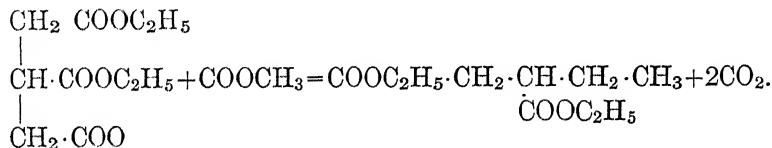
**Racemic Acid.**—The same investigators found that *racemic acid*, on electrolysis of the sodium salt in aqueous solution, gives carbon mon- and dioxides and an aldehyde which was not further investigated.

**Ethyltartaric Acid.**—This gave the same gases, but any other substances which may have been formed were not identified.

**Methanetricarboxylic Acid.**—Mulliken<sup>1</sup> employed the method, which has already been discussed (p. 104), in the electrolysis of the sodium salt of the triethyl ester of this acid and obtained ethanhexacarboxylic ester, besides some malonic ester. Further oxidation caused the formation of sodium bicarbonate:



**Tricarballic Acid.**—The potassium salt of the diester of this acid was subjected by von Miller<sup>2</sup> to the Brown-Walker reaction, but without success. The ester-acid was in part regenerated. When potassium acetate, however, was added to the anode solution the expected reaction occurred; ethylsuccinic ester was produced:



The peculiar fact that the di-esters of tricarballic acid, when electrolyzed by themselves, do not afford the expected synthetic reaction, while the electrolysis of a mixture of the acid with potassium acetate gives these synthetic products, was made use of by von Miller with several aromatic acids which had previously proven unsuitable for synthesis when used alone (see these).

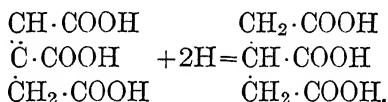
<sup>1</sup> Am. Chem. Journ. **15**, 323 (1893)

<sup>2</sup> Ztsch. f. Elektrochemie **4**, 55 (1897).



**Aconitic Acid.**—On electrolyzing a concentrated, strongly alkaline solution of the potassium salt, Berthelot <sup>1</sup> observed oxygen, carbon monoxide, and a little acetylene at the anode.

Marie <sup>2</sup> was able to convert aconitic acid into tricarballic acid at a mercury cathode surrounded with a solution of the acid half neutralized with sodium hydrate. Sixty per cent of the theoretical yield was obtained:

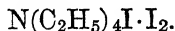


#### 7. AMINES, ACID AMIDES, IMIDES, AND NITRILES.

The literature on these subjects is very scarce. Little is known regarding the electrolysis of amines, whose anodic behavior would probably be very interesting. They are stable at the cathode, and can be obtained electrolytically by reduction of the nitriles. Weems <sup>3</sup> has electrolyzed acid amides in the form of their sodium or mercury compounds. He obtained only the unchanged material used as the starting-point.

**Tetramethylammonium Hydrate.**—Palmaer <sup>4</sup> electrolyzed a solution of the hydrate in liquid ammonia in a Dewar vessel at about  $-41^\circ$ . Deep-blue rings having the color of a solution of sodium in liquid ammonia appeared at the cathode when the circuit was closed. A solution of free tetramethylammonium is probably formed, which could not be isolated. The chloride behaves like tetramethylammonium hydrate.

**Tetraethylammonium Chloride.**—Goecke <sup>5</sup> has investigated the behavior of the iodide of this compound in aqueous solution. He found at the anode tetraethylammonium triiodide:



<sup>1</sup> Compare Bourgoin, Bull. soc. chim. [2] 9, 103 (1868).

<sup>2</sup> Compt. rend. 136, 1331 (1903).

<sup>3</sup> Am. Chem. Journ. 16, 569 (1894).

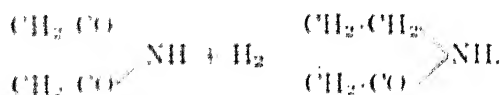
<sup>4</sup> Ztschr. f. Elektrochem. 8, 729 (1902).

<sup>5</sup> Ibid. 10, 250 (1904).

The yield was 40% of the material used as the starting-point. A little isoform is also produced, by the action of iodine on portions of the original iodide destroyed by oxidation.

The method of Tafel (p. 23), which has been discussed in the theoretical part, has also done good service in the reduction of succinimide and some of its derivatives. This method, for reducing in sulphuric-acid solution substances reducible with difficulty, has also proven very fruitful in the domain of the carbonic acid derivatives and of the alkaloids.

**Succinimide.** Tafel and Stern,<sup>1</sup> by reduction of this substance in a 50% sulphuric acid, obtained about 60% of a yield of pyrrolidone. The fluid was kept cold and electrolyzed at high current densities:



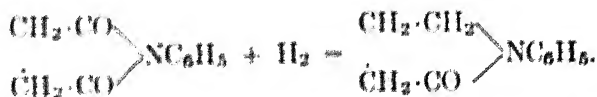
Fairly large quantities of substances having higher boiling-points, but which do not boil without decomposition, are also produced.

The reduction of

**Isopropylsuccinimide**, likewise electrolyzed, gave a yield of about 80% of the theoretical of isopropylpyrrolidone:



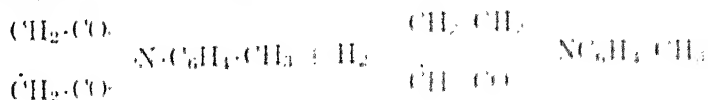
**Succinanil** was converted by the same method (Baillie and Thomas<sup>2</sup>), but in *concentrated* sulphuric acid, into phenylpyrrolidone:



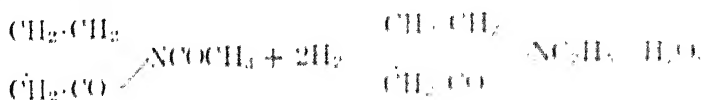
<sup>1</sup> Ber. d. deutsch. chem. Gesellsch. **33**, 2224 (1900)

<sup>2</sup> Ibid **32**, 68 (1899)

A moderate yield of *p*-tolylpyrrolidone is obtained from *p*-tolylsuccinimide in 95% sulphuric acid:



Acetylpyrrolidone can be reduced to ethylpyrrolidone in a 50% sulphuric acid (Tafel and Stern<sup>1</sup>):



**Hydrocyanic Acid.** In sulphuric acid solution hydrocyanic acid breaks up smoothly, according to Gay Lussac<sup>2</sup> into hydrogen and cyanogen. Concentrated hydrocyanic acid to which a drop of sulphuric acid has been added gives carbon monoxide and ammonia (Schlagdenhauffen<sup>3</sup>).

**Potassium Cyanide.** In the investigation of this salt, conducted by the author last mentioned, it was found that no oxygen escaped at the anode, but the potassium cyanide was oxidized to potassium cyanate. Bartoli and Papareggi obtained mellogene from potassium cyanide by using carbon anodes, and mellitic acid at graphite anodes.

**Potassium Ferrocyanide.** This compound gives at the anode hydrocyanic acid and Prussian blue, and at the cathode hydrogen and potassium hydroxide (Perrot<sup>4</sup>); also cyanogen (Schlagdenhauffen<sup>5</sup> and Schönbein).

**Potassium Ferricyanide** on electrolysis likewise gives Prussian blue<sup>6</sup> at the anode, being the first electrolytic oxidation product of potassium ferrocyanide.

**Sodium Nitroprusside.**—On electrolyzing a dilute solution of this salt for a prolonged period, Weith<sup>7</sup> noted the formation of

<sup>1</sup> l. c.

<sup>2</sup> Ann. chim. phys. 78, 245 (1811).

<sup>3</sup> Jahresb. f. Chem. 1863, 305.

<sup>4</sup> Tommasi, Traité d'Electrochimie 729.

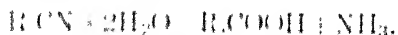
<sup>5</sup> Journ. f. prakt. chemie 30, 145 (1843).

<sup>6</sup> Eng. Pat. No. 7126 (1890); Elect. Review 32, 216 (1893).

<sup>7</sup> Jahresb. f. Chem. 1863, 306, 1868, 311.

ammonia and precipitation of metallic iron; at the positive electrode Prussian blue appeared, and nitrogen, oxygen, and, if the operation was long continued, nitric oxide, also, were given off. In a concentrated solution much ammonia was formed at the cathode, and nitric oxide appeared at the anode.

**Nitriles.** Alcock<sup>1</sup> by means of the electrolytic addition of hydrogen, succeeded in converting nitriles into primary amines, while simultaneously with the reduction a partial saponification of the nitriles occurred, as represented by the following equation:

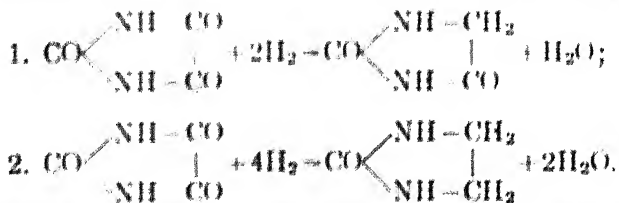


**Acetonitrile.** This substance in sulphuric-acid solution yields only a small quantity of ethylamine, although a considerable quantity of *n*-propylamine is formed from *n*-propyl-nitrile.

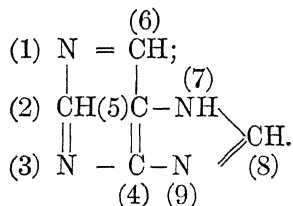
The reduction of *aromatic nitriles* takes place without the occurrence of secondary reactions. This is illustrated in the formation of benzylamine from *benzonitrile* and of phenyl-ethylamine from *benzophenone*.

### 8. CARBONIC ACID DERIVATIVES.

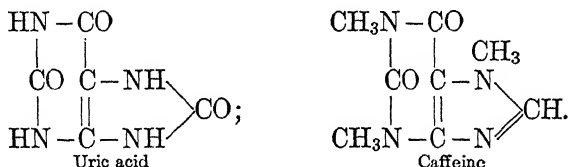
Tafel and his school have investigated the uric-acid group, which includes the ureides of dibasic acids, as to its behavior when electrolytically reduced at lead cathodes in sulphuric-acid solution. All members of this group belong to the difficultly reducible substances; the electrolytical effect can often not be attained by chemical means. The reduction does not affect the urea-group, but does act on the ketone-groups and the double bonds of the radicals united with the carbamide-molecule. Thus parabanic acid is converted into hydantoin and ethylene-urea.



E. Fischer claims that the members of the uric-acid group can be considered as derived from purin, a parent substance:



Accordingly, uric acid appears as 2, 6, 8-trioxypurin, and caffeine as 1, 3, 7-trimethyl-2, 6-dioxypurin:



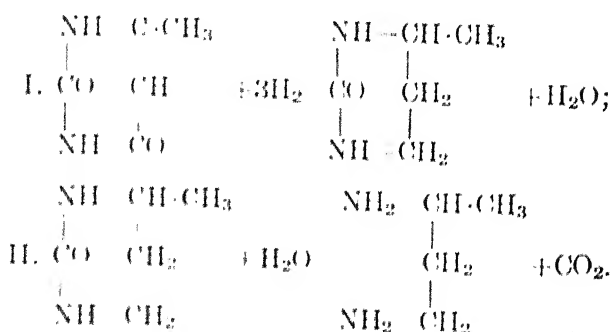
In the electrolytical reduction of the investigated purin derivatives, it appeared that the oxygen in position (6) of the purin nucleus is the only one that can be eliminated for hydrogen. But an addition of hydrogen occurs also without a loss of oxygen; this happens in the conversion of uric acid into tetrahydrouric acid. Further particulars will be mentioned under the individual substances.

**Parabanic Acid**, the ureide of oxalic acid and oxidation product of uric acid obtained by the action of nitric acid, is converted into hydantoin and ethyl urea (Tafel and Reindl<sup>1</sup>).

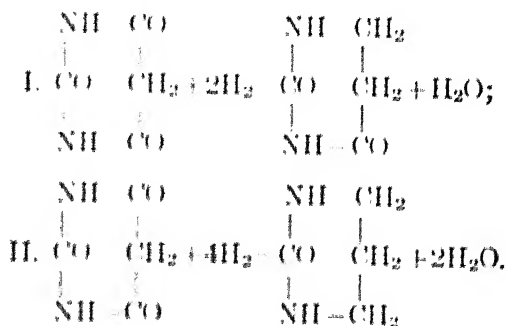
**Methyluracyl**, the reaction product of acetoacetic ester and urea (water and alcohol being eliminated), can be easily reduced in sulphuric-acid solution (Tafel and Weinschenk<sup>2</sup>). Methyl-trimethylene urea is formed, also a considerable quantity of 1.3-diaminobutane:

<sup>1</sup> Ber. d. deutsch. chem. Gesellsch. **34**, 3286 (1901).

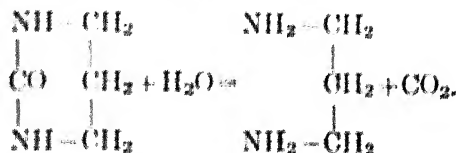
<sup>2</sup> Ibid. **33**, 3378 (1900).



Barbituric Acid, *Malonyl Urea*, was investigated by the same authors. It likewise gives two products, hydrouracyl and trimethylene urea:

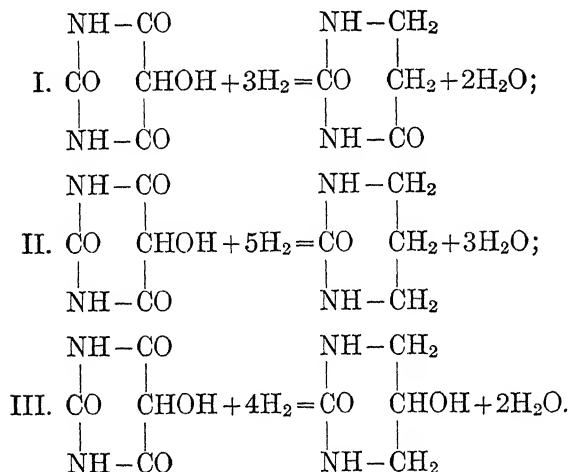


The convertibility of malonyl urea into trimethylene urea taken in connection with the decomposability of the cyclical ureas into diamines and carbonic acid affords a simple method of obtaining 1,3-diaminopropane from malonic acid in the same manner as 1,3-diaminobutane is produced from methyl uracyl:

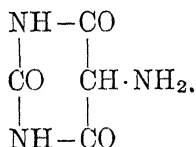


**Dialuric Acid, Tartronyl Urea.**—Tafel and Reindl<sup>1</sup> reduced this substance and obtained as chief reduction product hydrouracyl, also some trimethylene urea and oxytrimethylene urea:

<sup>1</sup> Ber. d. deutsch. chem. Gesellsch. 33, 3383 (1900).

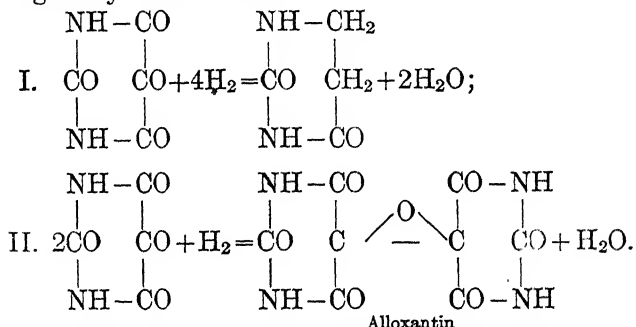


Uramil is the reduction product of violuric acid, which is the isonitroso-compound of barbituric acid:



It is easily reducible, ammonia being split off, and forms hydro-uracyl<sup>1</sup> as the solely crystallizable body. The same product is derived in considerable quantity in the electrolytic reduction of

**Alloxan, Mesoxalyl Urea.** There are also produced in this reduction alloxantin, which is difficultly soluble and can only slowly be reduced further, and large quantities of non-crystallizable gummy substances:



Alloxantin

<sup>1</sup> Ber. d. deutsch. chem. Gesellsch. **34**, 3290 (1901).

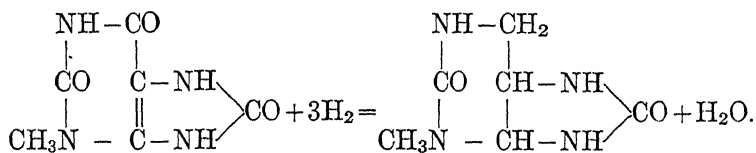




The structure of the last-mentioned acid has not yet been determined with certainty.<sup>1</sup>

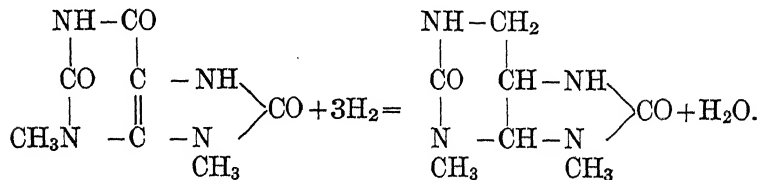
Strange to state, the methylated uric acids, when reduced, do yield purons which (excepting tetramethylpuron) can be molecularly rearranged into isomeric isopurons, but the corresponding hydrated uric acids are not produced (Tafel<sup>2</sup>).

**3-Methyluric Acids.**—The two isomeric and structurally identical 3-methyluric acids, the  $\delta$ - and  $\zeta$ -acids, give 3-methylpurons. These latter are extremely similar, but show differences in solubility which point to the possibility of an isomerism. A certain quantity of isopurons was already formed during electrolysis by the rearranging action of the 60-70% sulphuric acid used as electrolyte:



**1.3-Dimethyluric Acid.**—The reduction to 1.3-dimethylpuron takes place very slowly in a 75% sulphuric acid solution. The molecular rearrangement to isopuron is also very slow.

**3.9-Dimethyluric Acid** gives similarly a 3.9-dimethylpuron which, if heated in a 10% sodium-hydrate solution, smoothly rearranges itself to form the iso-compound. The electrolytical effect is hence a normal one:



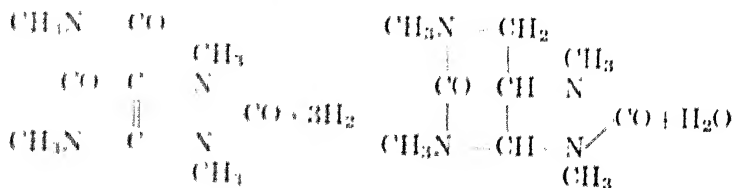
**7.9-Dimethyluric Acid** gives correspondingly a 7.9-dimethylpuron.

<sup>1</sup> Ber. d. deutsch. chem. Gesellsch. **34**, 1181 (1901).

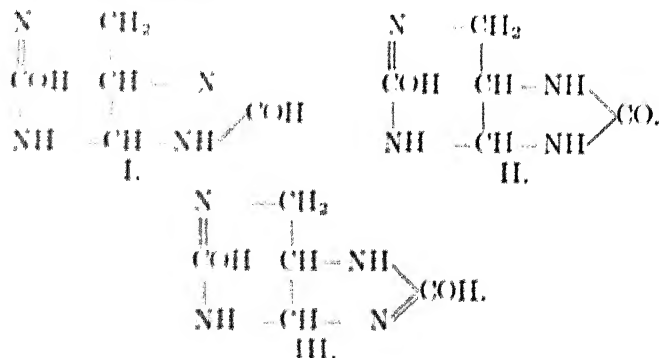
<sup>2</sup> Ibid., 279 (1901).

**1,3,7-Trimethyluric Acid**, or Hydroxycaffeine, is changed into 1,3,7-trimethylpuron by electrolytic reduction in 60% sulphuric acid. A good yield is obtained. By hydrochloric acid, and also by heating in a 10% sodium-hydroxide solution, it is converted into the trimethylisopuron.

**Tetramethyluric Acid.** This substance, by reduction in 50% sulphuric acid, is changed to tetramethylpuron. The latter does not rearrange itself.



Tafel has proposed the following three formulas for isopuron:

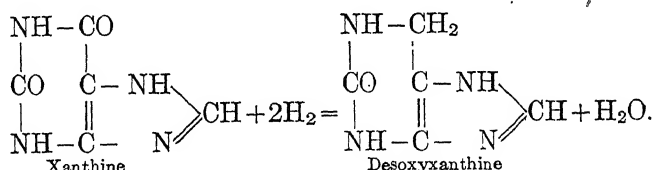


Tafel has also successfully reduced the xanthine bases: Guanine, xanthine, theobromine, caffeine, adenine and hypoxanthine, or sarcine. The electrolyte was a sulphuric-acid solution, and lead cathodes were employed.

The effect consists in the addition of two hydrogen atoms and the elimination of an atom of oxygen. Tafel calls the reduction products *desoxy-bodies*. Their formation is characteristic of the xanthine bases.

**Xanthine**, on reduction in 75% sulphuric acid, yields desoxyxanthine. The yield is 70% of the theoretically possible

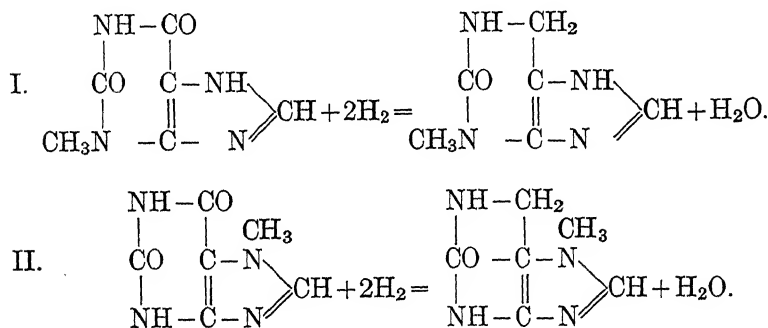
quantity. The reaction takes place in accordance with the following equation:



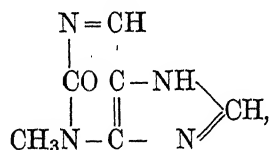
The latter compound is therefore to be regarded as 2-oxy-1.6-dihydropurin. These experiments were made by Tafel and Ach.<sup>1</sup>

**3-Methylxanthine** gives analogously 3-methyldesoxyxanthine or 3-methyl-2-oxy-1.6-dihydropurin (Tafel and Weinschenk<sup>2</sup>), and

**Heteroxanthine**, 7-Methylxanthine, yields desoxyheteroxanthine, or 7-methyl-2-oxy-1.6-dihydropurin:



If desoxy-compounds are suitably oxidized, they lose two atoms of hydrogen and pass into oxypurins. 3-Methyldesoxyxanthine is thus converted into 3-methyl-2-oxypurin:

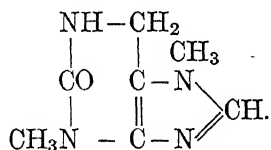


<sup>1</sup> Ber. d. deutsch. chem. Gesellsch. **34**, 1165 (1901).

<sup>2</sup> Ibid. **33**, 3369 (1900).

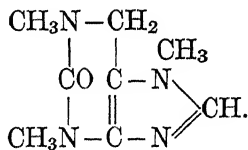
and desoxyheteroxanthine gives the corresponding 7-methyl-2-oxypurin. These oxidation products furnish the proof of the constitution of desoxy-compounds. The constitution for some of the members had been determined by E. Fischer through synthesis.

**Theobromine**, or 3,7-Dimethylxanthine, was reduced by Tafel<sup>1</sup> in 50% sulphuric acid. He obtained desoxytheobromine, or 3,7-dimethyl-2-oxy-1,6-dihydropurin:

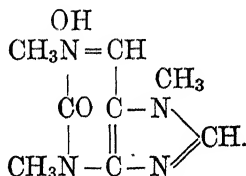


3,7-Dimethyl-2-oxypurin is formed on oxidation with an excess of silver acetate.

**Caffeine**, or 1,3,7-Trimethylxanthine, was reduced in 50% sulphuric acid to desoxycaffeine by Tafel and Baillie,<sup>2</sup> while they were investigating the reduction of acylamines to alkylamines. In a later investigation<sup>3</sup> they showed that desoxycaffeine is to be designated as 1,3,7-trimethyl-2-oxy-1,6-dihydropurin:



By oxidizing it with lead peroxide, 3,7-dimethyl-2-oxypurin-1-methylhydroxide is obtained:



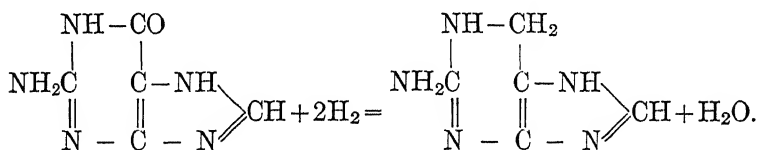
<sup>1</sup> Ber. d. deutsch. chem. Gesellschaft. **32**, 3194 (1899).

<sup>2</sup> Ibid., 686 (1899).

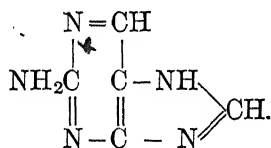
<sup>3</sup> Ibid., 3206 (1899).

This is a compound which corresponds to the 3-methyl-2-oxypurin obtained from 3-methyldesoxypurine. Its strongly basic properties are conditioned by the methyl group in position (1). It may be here mentioned that Tafel has worked out his valuable method chiefly by the use of caffeine. The corresponding investigation has already been considered (p. 24 and p. 52).

**Guanine**, 2-amino-6-oxypurin, when electrolytically reduced in a 60% sulphuric acid, is converted into desoxyguanine, a base containing no oxygen (Tafel and Ach<sup>1</sup>):



Desoxyguanine, 2-amino-1,6-dihydropurin, is easily oxidized to 2-aminopurin:



This substance is isomeric with adenine and is very similar to it. Nitrous acid converts it into 2-oxypurin, an isomer of hypoxanthine.

The firm of C. F. Boehringer & Söhne (Waldhof-Mannheim) has patented<sup>2</sup> Tafel's process for reducing xanthine bases.

## 9. DERIVATIVES OF CARBONIC ACID CONTAINING SULPHUR.

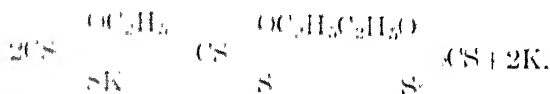
**Potassium Xanthate.**—C. Schall<sup>3</sup> obtained, by the electrolysis of potassium xanthate in aqueous solution and with

<sup>1</sup> Ber. d. deutsch. chem. Gesellsch. **34**, 1170 (1901).

<sup>2</sup> See especially D. R. P. No. 108577 (1898): Process for the preparation of xanthines containing less oxygen by means of the electrolytic reduction in acid solution of alkylated xanthines.

<sup>3</sup> Zeitschr. f. Elektrochemie **2**, 475 (1896); **3**, 83 (1897).

a high anode current density, xanthic supersulphide, or ethyl dioxysulphocarbonate, as might be expected:

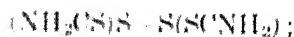


**Potassium Methyl-, Isobutyl-, and Isoamylxanthate** behave analogously (Schall and Kraszler<sup>1</sup>). They are converted at the anode into the corresponding dithiondisulphides



These are non-crystallizable oils.

**Ammonium Dithiocarbamate** is converted with difficulty into thiuramdisulphide:



the conditions under which this takes place have not yet been explained.

**Diethylammonium Diethyldithiocarbamate** is said to give at the anode tetraethylthiuramdisulphide:



**Potassium Ethyltrithiocarbonate** gives dithiondisulphide:



**Potassium Phenylsulphocarbazine**,  $\text{C}_6\text{H}_5\text{NH}\cdot\text{NHCSSK}$ , gives (Schall and Kraszler<sup>2</sup>) no disulphide, but diphenylthiocarbazine:



<sup>1</sup> Zeitschr. f. Elektrochemie 5, 223 (1908).

<sup>2</sup> l. c.

## CHAPTER IV.

### THE ELECTROLYSIS OF AROMATIC COMPOUNDS.

In the aliphatic series the carboxylic acids furnish the principal material of electrolysis. This is due to the reactivity of their anions, which readily split off carbonic acid, thus affording manifold syntheses. In the aromatic series, however, the nitro-compounds are the more interesting, on account of their easy reducibility and the importance of their reduction products. The facts which give to electrochemical reduction pre-eminence over oxidation have already been explained in the introduction (p. 2).

Single oxidation processes have, however, also become important. Besides the oxidability of easily oxidizable substances, for instance aniline, or easily oxidizable groups like methyl, the peculiar reaction which seems to occur very frequently in the electrical oxidation in sulphuric acid, and which consists of the entrance of oxygen into the benzene nucleus, must be emphasized. Hydrocarbons, phenols, quinones, and azo-compounds seem to behave alike in this respect.

Electrolytic substitutions furnish a further general point of view.

Although the substitution processes afforded by the action of the primarily discharged anion of an inorganic salt upon an organic body are to be included among the simpler reactions, the results obtained so far in this domain have been very scanty, especially in regard to aromatic substances. The above-mentioned investigations of Elbs and Hertz, as well as those of Förster and Mewes on the electrolytic preparation of iodoform,

can serve as an indication that many interesting and remunerative problems yet await solution in this field.

### 1. HYDROCARBONS.

**Benzene.**—Renard,<sup>1</sup> by the anodical action of the current in an alcohol-sulphuric-acid solution of benzene with platinum anodes, obtained a body melting at 171° which Gattermann and Friedrichs<sup>2</sup> recognized later as hydroquinone. The latter is also formed (Kempf<sup>3</sup>) if a mixture of benzene and a 10% sulphuric acid is electrolyzed at lead-peroxide anodes and lead or zinc cathodes. Quinone is first produced at the anode with the aid of the lead peroxide. It is then reduced at the cathode to hydroquinone.

The process very likely occurs in the same way at a platinum anode. Hydroquinone itself, when oxidized electrolytically, yields only traces of quinone (Liebermann<sup>4</sup>), quinhydrone being the chief product.

However, it is not impossible that at platinum anodes a direct introduction of hydroxyl groups into the benzene nucleus, i.e. a primary formation of hydroquinone, takes place, especially if concentrated sulphuric acid is chosen as the electrolyte. Chemical as well as electrochemical experiences indicate this. Thus, by means of persulphuric acid or its salts, obtained by the electrolysis of sulphuric acid or its salts, nitrophenol can be directly converted into nitrohydroquinone, salicylic acid into hydroquinonecarboxylic acid, anthraquinone into alizarin, and this latter into alizarin-bordeaux and alizarin-cyanine.

It may be here mentioned that oxygen can thus be electrolytically introduced into azobenzene. Heilpern,<sup>5</sup> by electrolyzing azobenzene in concentrated sulphuric acid, obtained tetraoxy-

<sup>1</sup> Compt. rend. **91**, 175 (1880).

<sup>2</sup> Ber. d. deutsch. chem. Gesellsch. **27**, 1942 (1894).

<sup>3</sup> D. R. P. No. 117251 (1899).

<sup>4</sup> Ztschr. f. Elektrochemie **2**, 497 (1896).

<sup>5</sup> Ibid. **4**, 89 (1879).



azobenzene, a fast dye, soluble in concentrated sulphuric acid with a cherry-red color and resistant to the action of light and acids.

**Toluene.**—According to Renard,<sup>1</sup> this compound, by electrolytic oxidation in alcoholic-sulphuric acid, forms benzaldehyde and phenose,  $C_6H_6(OH)_6(?)$ . According to Puls,<sup>2</sup> there are produced in the same electrolyte, using a diaphragm and a platinum anode, benzaldehyde, benzoic acid, benzoic ethyl ester, and, as chief product, p-sulphobenzoic acid. Under the same conditions, Merzbacher and Smith<sup>3</sup> had obtained a poor yield of benzoic ethyl ester.

Law and Mollwo Perkin<sup>4</sup> report on the electrolytic oxidation of toluene, the three *xylenes*, *mesitylene*, and *pseudocumene*. In a sulphuric-acid-acetone solution of toluene they obtained a little benzaldehyde and perhaps benzyl alcohol. The electrolysis of an emulsion of toluene and dilute sulphuric acid leads to a complete combustion of the toluene to carbonic acid and water.

The three *xylenes*, electrolyzed in acetone and dilute sulphuric acid, yield principally the three toluic aldehydes. m-Xylene, even when sodium acetate and acetic acid are employed as electrolyte, gives the m-toluic aldehyde.

Pseudocumene, in the presence of acetone and sulphuric acid, gives apparently a mixture of the three isomeric dimethylbenzaldehydes. Analogously, mesitylene is oxidized to mesitylenic aldehyde.

**Naphthalene.**—This substance, electrolyzed by Panchaud de Bottens<sup>5</sup> in a sulphuric-acid-acetone solution at platinum and lead anodes, gives, besides a brown by-product, principally a little  $\alpha$ -naphthoquinone. In glacial-acetic-sulphuric acid traces of phthalic acid are formed at platinum electrodes.

<sup>1</sup> Compt. rend. **91**, 175 (1880).

<sup>2</sup> Chem. Ztg. **25**, 263 (1901).

<sup>3</sup> Journ. Am. Chem. Soc. **22**, 723 (1900).

<sup>4</sup> Trans. of the Faraday Soc. I (25/10, 1904).

<sup>5</sup> Ztschr. f. Elektrochemie **8**, 673 (1902).

## 2. NITRO- AND NITROSO-COMPOUNDS.

Of all organic substances which have been tested as to their behavior towards the action of the electric current, aromatic nitro-compounds have received the most accurate treatment and attained the greatest importance. The reason for this lies, on the one hand, in the fact that the nitro-group, being extremely reducible, reacts only at the cathode, whereby the end-products are closely and simply related to the product started with; and, on the other hand, in the variety of the reduction phases which the nitro-group can develop, depending upon the conditions of the experiment.

It thus happens that the class of nitro-bodies not only affords the greatest number of important results and smooth reactions, and thereby is of great importance technically and for the manufacturing side of organic chemistry, but it also offers the suitable starting-point for the treatment of general and special theoretical questions. So far as these are of a general nature, treating of the relation of the reaction velocity to the reduction velocity and referring to the importance of the cathode material, they have already been discussed in the first chapter. The theoretical relations, which are of importance only for the reduction of nitro-bodies, will be briefly considered here. They can be divided into purely chemical and electrochemical ones. The former, which obtain in every method for the reduction of nitro-bodies, deserve mention because they were first understood in closest connection with the *electrical* reduction; they refer to chemically possible reduction phases and their gradation. The latter encompass the dependence of the chemical results upon the electrical conditions of experiment and the special rôles of the separate decisive factors.

The importance, thus shown, of our knowledge of the electrical reduction of nitrobenzene in regard to the practical and theoretical exploitation of the electrolysis of organic substances makes it desirable to first give a short historical survey

of the development of the views and the importance of the separate observations.<sup>1</sup>

*a. General Observations on the Reduction of Nitro-compounds.*

Häussermann<sup>2</sup> reduced *nitrobenzene* and *nitrotoluenes* both in alkaline and acid solution, the former with iron, the latter with platinum, electrodes. By reduction in alkaline solution, he obtained as principal product *hydrazobenzene* and *hydrazotoluene* respectively; in sulphuric-acid solution he got from nitrobenzene, as chief products, *benzidine sulphate* and *azoxybenzene*, besides an easily changeable body which was not further determined. *o*-Nitrotoluene<sup>3</sup> under like conditions gave *o*-toluidine sulphate, besides small quantities of *o*-toluidine; *p*-nitrotoluene yielded principally *p*-toluidine.

Elbs, on the contrary, obtained entirely different results when he electrolytically reduced *p*-nitrotoluene and nitrobenzene in acid and in alkaline solution with other cathode metals. There were formed in the reduction of nitrobenzene in alkaline solution at a lead or mercury cathode varying quantities of *azoxy*- and *azobenzene*, the former mostly preponderating. *p*-Nitrotoluene behaves similarly if reduced in the same manner, —*p*-azoxy- and *p*-azotoluene being produced. The reduction takes place much more slowly and less completely in this case than when nitrobenzene is used. Häussermann observed the same with *o*-nitrotoluene. *o*-Nitrophenol behaves quite differently; the chief product is *o*-amidophenol, besides red and brown substances which could not be obtained pure. In the reduction of nitrobenzene in sulphuric-acid solution Elbs employed a zinc cathode and obtained chiefly *aniline*.

Elbs<sup>4</sup> draws the following conclusion: "Without considering the other conditions of experiment, the kind of metal

<sup>1</sup> This classification (*a*) has been partially taken from the dissertation of my pupil Jos. Schmitt: "Concerning the Importance of the Cathode Material in the Electrolytic Reduction of *m*- and *p*-Nitrotoluene," Bonn, 1904.

<sup>2</sup> Chem. Ztg. 17, 129, 206 (1893).

<sup>3</sup> Ibid., 209 (1893).

<sup>4</sup> l. c.

employed as electrode seems to exert an important influence, since Häussermann obtained benzidine and azoxybenzene from nitrobenzene at a platinum electrode." Gattermann and Koppert,<sup>1</sup> by electrolytically reducing nitrobenzene in concentrated sulphuric acid with the addition of a few drops of water, obtained other results. After several hours' electrolysis the contents of the earthenware cell, which contained the reduction fluid together with a platinum cathode, solidifies, forming a colorless mass of crystals of p-amidophenol sulphate, which was permeated by a blue-green liquid.

After these observations, Gattermann and his pupils<sup>2</sup> continued their investigation on the reduction of aromatic nitro-bodies to amidophenol derivatives. They thus examined mono- and dinitrohydrocarbons, nitroamines, nitrocarboxylic and nitrosulphonic acids, also the esters of the acids. After the reaction had been successfully tested in over 40 cases it was adjudged to be of general applicability.

The important result of these experiments is that nearly all nitro-bodies with an unoccupied para-position are converted by electrolytic reduction in concentrated sulphuric acid into p-amidophenol derivatives, i.e. not only is the nitro-group reduced completely to the amido-group, but in most cases the hydrogen atom in p-position to the amido-group is simultaneously substituted by the hydroxyl group.

A short time after the publication of the interesting experiments of Gattermann, A. A. Noyes and A. A. Clement<sup>3</sup> made known their studies on the electrolytic reduction of nitrobenzene in sulphuric-acid solution.

Noyes and Clement used concentrated sulphuric acid of 1.84 to 1.94 sp. gr. as a solvent for nitrobenzene. Gattermann and Koppert had treated the sulphuric-acid solution before the reduction with a few drops of water. Noyes and Clement obtained from 50 g. nitrobenzene at platinum electrodes 30 g. anhydrous p-amidophenol-o-sulphonic acid, cor-

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<sup>1</sup> Chem. Ztg. 17, 210 (1893).

<sup>2</sup> Ber. d. deutsch. chem. Gesellsch. 26, 1844, 2810 (1893); 27, 1927 (1894).

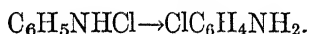
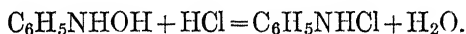
<sup>3</sup> Ibid 26, 990 (1893).

responding to a yield of 40 per cent. of the theoretically possible quantity.

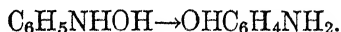
Three years later Elbs<sup>1</sup> reverted to the experiments of Gattermann. On repeating the same he obtained, indeed, the same results, but simultaneously observed that considerable quantities of aniline are always formed besides the p-amidophenol. When Elbs used glacial acetic acid as a diluent of the sulphuric acid he found a considerable increase in the yield of p-amidophenol, but the yield of aniline kept apace of that of the latter. If he used a lead in place of a platinum cathode, the reduction was accelerated, being favorable to the aniline formation at the expense of the p-amidophenol.

Löb<sup>2</sup> found a reaction analogous to that of Gattermann when he reduced nitrobenzene in hydrochloric-acid solution or suspension, using platinum electrodes.

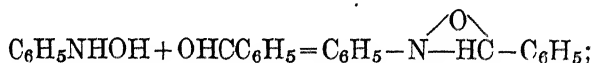
In this process there is formed as chief product a mixture of o- and p-chloraniline. The formation of this can be explained thus: The primarily formed phenylhydroxylamine reacts with the hydrochloric acid, simultaneously rearranging itself:



The same mechanism of molecular rearrangement must be assumed in Gattermann's reaction:



Direct proof of the correctness of this view was produced by Gattermann<sup>3</sup> on adding benzaldehyde to the solution of nitrobenzene in sulphuric acid. Benzylidenephénylhydroxylamine is formed:



<sup>1</sup> Ztschr. f. Elektrochemie 2, 472 (1896).

<sup>2</sup> Ber. d. deutsch. chem. Gesellsch. 29, 1894 (1896).

<sup>3</sup> Ibid., 3034, 3037, 3040 (1896).

i.e. the condensation product of phenylhydroxylamine with benzaldehyde.

A similar influence of the cathode material, as observed by Elbs in replacing the platinum electrode by a lead cathode in sulphuric-acid solution, was found by Löb<sup>1</sup> when he used a lead cathode in hydrochloric-acid solution. No chloraniline was formed, aniline being produced almost exclusively.

Further observations concerning the influence of the cathode material in reductions were made by Löb<sup>2</sup> in his studies on the electrolytic preparation of benzidine. His results are briefly the following:

1. Platinum and nickel electrodes behave alike in the experiments to reduce nitrobenzene in acid solution to benzidine. Carbon cathodes, on the contrary, give only little benzidine; zinc and amalgamated zinc electrodes yield no, or extremely little, benzidine, while aniline, as already previously observed by Elbs, results as the principal product.

2. Mercury, nickel, copper, zinc, lead, iron, brass, and zinc amalgam were tried as electrode material in respect to their reduction behavior in the reduction of azobenzene to benzidine in alcohol-sulphuric-acid solution. It was shown that the furthest utilizable reduction was obtained with mercury; the usefulness of the other metals was determined to be in the following order: Lead, sheet nickel, nickel-wire gauze, copper, zinc, iron, and brass.

3. In the reduction experiments of nitrobenzene to azobenzene in alkaline-alcoholic solution mercury electrodes prove good; however, nickel-wire-gauze electrodes give excellent results. This had been already shown by Elbs.<sup>3</sup>

4. The same is true in the reduction of nitrobenzene to azoxybenzene in an alkaline aqueous suspension.

Finally, the employment of a strong hydrochloric acid and a tin cathode, or an unattackable cathode with addition of

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<sup>1</sup> *Ztschr. f. Elektrochemie* 4, 430 (1898).

<sup>2</sup> *Ibid.* 7, 337, 597 (1900-1901).

<sup>3</sup> *Ibid.* 5, 108 (1898).

stannous chloride, was ascertained to constitute a favorable condition for the reduction of azoxybenzene and azobenzene to benzidine.

The practical results of all these investigations for the reduction of nitrobenzene and its reduction phases are briefly the following:

At attackable electrodes, like zinc, lead, and tin, the reduction generally proceeds further than at unattackable electrodes such as platinum, nickel, and mercury. The attempts to utilize technically these properties of the cathode metals in a series of nitro-bodies led to important patents.

Thus Boehringer & Söhne<sup>1</sup> (Mannheim) patented a process by which, when employing tin-cathodes (or cathodes of other indifferent metals with an addition of a small quantity of tin salt), fatty or aromatic nitro-compounds, dissolved or suspended in aqueous or hydro-alcoholic hydrochloric acid, can be reduced in almost theoretical yields to the corresponding amines.

In hydrochloric-acid solution, as already mentioned, chloroanilines are produced at platinum electrodes.

According to another patent<sup>2</sup> of the same firm, copper, lead, iron, chromium, and mercury can be used instead of tin if these metals are added in the form of their salts or as a finely divided powder to the cathode electrolyte.

After the publication of these patents Elbs and Silbermann reported that if a lead cathode in sulphuric acid is employed the same results are attained. It proved to be true that in order to obtain the best yields of aniline diluted alcohol serves as a better diluent for the sulphuric acid than the glacial acid formerly employed. Zinc behaves in sulphuric-acid solutions like lead; however, the precipitation of difficultly soluble zinc double salts is a hindrance. Elbs likewise obtained 90 per cent of the theoretical yield of toluidines from o- and

<sup>1</sup> D. R. P. No. 116942 (1899).

<sup>2</sup> D. R. P. No. 117007 (1900).

<sup>3</sup> Ztschr. f. Elektrochemie 7, 589 (1901).

m-nitrotoluene; the yield from p-nitrotoluene was a few per cent. less.

A supplementary patent of Boehringer & Söhne<sup>1</sup> extends the process of the D. R. P. No. 116942 to the reduction of azo-bodies to amines.

The patent claim is as follows: "Process for the reduction of azo-bodies to the corresponding amines; consisting in reducing azo-bodies in acid solution by simultaneously conducting a constant electric current either with a tin cathode, or with an indifferent cathode and the addition of a tin salt or pulverized metallic tin."

In a later patent<sup>2</sup> C. F. Boehringer & Söhne point out that the nitro-compounds in acid solution can not only be reduced to amines with such metals as easily evolve hydrogen with dilute acids, but also with copper. This fact offers particular technical advantages, because copper can be most easily and completely regenerated electrolytically from the liquors. While in the above-mentioned methods the reduction to the amines is made in acid solution, C. F. Boehringer & Söhne have obtained a patent<sup>3</sup> according to which it is also possible to reduce nitro-bodies to the corresponding amines in alkaline and alkali-salt suspension, if a copper cathode with or without the addition of copper powder is employed.

According to an investigation by Elbs and Brand,<sup>4</sup> the addition of copper powder is absolutely necessary for obtaining the desired effect.

In 1899 the Farbenfabriken vorm. Friedr. Bayer & Co.<sup>5</sup> (Elberfeld) patented a process for electrolytically preparing azo- and hydrazo-compounds. The method is characterized by the fact that the nitro-body to be reduced is held suspended in the alkaline cathode liquid, and is reduced during continuous vigor-

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<sup>1</sup> D. R. P. No. 121835 (1900). See also the English Pat. No. 19879 (1901).

<sup>2</sup> D. R. P. No. 127815 (1901).

<sup>3</sup> D. R. P. No. 130742 (1901).

<sup>4</sup> Ztschr. f. Elektrochemie 8, 789 (1902).

<sup>5</sup> D. R. P. No. 121899 (1899).



ous stirring and the addition of a metallic oxide solution of zinc, tin, or lead.

This method was then extended by a supplementary patent,<sup>1</sup> according to which the reduction of aromatic nitro-bodies is carried out in aqueous alkaline suspension instead of in the presence of alkali-soluble oxides of the heavy metals and the use of such metal cathodes the oxides of which are soluble in alkalies.

It is very evident, from all these observations, what influence the cathode material exercises on the obtainable reduction phase of nitrobenzene and its derivatives. There is no lack of attempts to explain this influence. The expressed opinions can be grouped under three points of view:

1. The specific action of the cathode metal is a purely chemical function.
2. It is a purely electric function, and depends upon the potential values obtainable on the various metals.
3. A summation of electrical and chemical influences occurs.

Elbs<sup>2</sup> defends the first view. He explains the aniline formation at lead and zinc cathodes in sulphuric-acid solution in the following manner:

"We will have to suppose that the lead sponge occurring at the lead cathode reduces the nitrobenzene to aniline. Mentionable quantities of lead sulphate cannot be found, since this is continually reconverted to lead sponge by the freed hydrogen ions. This process is analogous to the one previously published by me<sup>3</sup> in which a hydro-alcoholic solution of nitrobenzene acidified with sulphuric acid gives aniline when a zinc cathode is used. Considerable quantities of zinc sulphate do not occur. At a platinum cathode, under the same conditions, no aniline is formed, but azoxybenzene and hydrazobenzene or benzidine form. This has been confirmed by Häussermann."<sup>4</sup>

The explanation attempted by Elbs agrees in general with

<sup>1</sup> D. R. P. No. 121900 (1899).

<sup>2</sup> Ztschr. f. Elektrochemie 2, 474 (1896).

<sup>3</sup> Chem. Ztg. 17, 209 (1893).

<sup>4</sup> Ibid., 129 (1893).

that advanced in the specifications of C. F. Boehringer & Söhne's patents, D. R. P. No. 116942 and No. 117007:

"If attackable cathodes of metallic tin are employed, tin is dissolved continually at the cathode during the simultaneous reduction of the nitro-body so long as unchanged nitro-compounds are present. The metal is, however, immediately precipitated again on the cathode in the form of spangles or mud. When an unattackable cathode, say nickel, is used, and stannous chloride added, metallic tin is first precipitated on the cathode; the process following then resembles the one above explained. A transition of positively laden tin ions from the cathode into the electrolyte follows, and a deposition of tin ions at the same place. Very small quantities of tin hence suffice for reducing any desirable quantity of a nitro-body."

Haber,<sup>1</sup> on the basis of extensive experiments, defends the opinion that only the cathode potential is decisive for the obtainable reduction phase. This investigator, by carrying out the reduction of nitrobenzene in acid and in alkaline solutions with variable and in several experiments constant cathode potentials, succeeded in proving that, depending upon the chosen cathode potential, the reduction can be directed at will to the several reduction stages. He was thus able to determine the dependence of the formation of phenylhydroxylamine, azoxybenzene, hydrazobenzene, and aniline upon the cathode potential, and thus obtained an insight into the reduction stages in the case of nitrobenzene. Aided by the researches of Bamberger, he was thus led to a clear understanding of the gradation occurring in the reduction of nitrobenzene.

Loh,<sup>2</sup> by reason of his experiments with Moore, coincides with Haber's opinion, but he proceeds from other considerations concerning the reduction mechanism (see p. 14).

The third opinion was advanced by Chilesotti<sup>3</sup> and Tafel.<sup>4</sup>

<sup>1</sup> *Ztschr. f. Elektrochemie* 4, 596 (1898); *Ztschr. f. phys. Chemie* 32, 193, 271 (1900).

<sup>2</sup> *Ztschr. f. phys. Chemie* 47, 418 (1904).

<sup>3</sup> *Ztschr. f. Elektrochemie* 7, 768 (1901).

<sup>4</sup> *Ztschr. f. anorg. Chemie* 21, 289 (1902).

According to this view, electrical and chemical reduction can be simultaneously active.

Chilesotti, in order to determine the primary chemical action of the metals, subjected nitrobenzene and nitrobenzylamine to aniline, formed intermediately in the course of the reaction, to the action of electrolytically prepared copper, iron, or nickel, in hydrochloric or sulphuric acid solution. The copper was always that formed at the cathode when a copper electrode is electrolysed or when a copper salt is added to the electrolyte. He found that, chemically, copper can reduce nitrobenzene, but with a very insignificant velocity; phenylhydroxylamine, on the contrary, was almost completely reduced to aniline in a very short time. He concludes: "Judging from these experiments, the progress of the reactions in the process for electrolytic reduction of nitro-compounds to anilines, primarily in the presence of copper or ferric salts, can be summed up in the following manner. The current at first reduces the nitrobenzene to phenylhydroxylamine (which also happens in the absence of the mentioned salts) and simultaneously deposits spongy copper or produces ferrous salt. These in turn now reduce, in a purely chemical way and during electrolysis (as shown by the experiments), the phenylhydroxylamine very rapidly to the aniline. Hence they again revert to the copper or ferric ion and are again subject to the current action. It remains an open question, and one that cannot at least be directly negatived, whether the current action can also at the same time and primarily effect the reduction of phenylhydroxylamine to the aniline at the cathode potential given by the copper or ferrous salt. Thus we can also suppose in the case of tin, lead, or zinc electrodes, that in their presence or in that of their salts the current can primarily form phenylhydroxylamine. The deposited metals can now reduce chemically both this compound and the nitro-compound. They would very likely prefer the former, since they could apparently carry out this reduction with the greatest velocity."

Tafel, by reason of his experiments on the reduction of nitric acid in the presence of sulphuric acid, is inclined to this view. He found that nitric acid in sulphuric-acid solution and at a

lead cathode is primarily reduced almost exclusively to hydroxylamine, which can only with great difficulty be changed electrolytically into ammonia. At copper electrodes ammonia exclusively is formed. Since nitric acid cannot be reduced to hydroxylamine to any appreciable extent chemically by copper, nor electrically at copper electrodes, Tafel supposes that an intermediate product is formed in the electrolysis of nitric acid; possibly dihydroxylamine  $\text{NH}(\text{OH})_2$  possesses the property of being chemically reduced by copper to ammonia. Thus the reduction to hydroxylamine would be a purely electrical process, while the formation of ammonia at copper electrodes depends on a combination of electrical and chemical reductions.

Two important results can be derived from all these investigations: The certain insight into the course of the reduction of the single phases and the clear knowledge of the importance of the cathode potential.

Since the decisive relations have been worked out with the simplest representative of a nitro-body, nitrobenzene, the necessary data on this substance will be discussed first, and these data will be supplemented so far as necessary under the derivatives of nitrobenzene.

### *b. The Reduction of Nitrobenzene.*

#### **I. Chemical Relations.**

The course of electrical reduction, like that of purely chemical reduction, depends decisively upon whether the reduction is carried out in an alkaline or acid solution. But these relations are of a positive nature in electrolysis only so long as they are not compensated by the electrical factors, such as cathode material and potential. To avoid a complication, it is necessary to limit the considerations primarily to unattackable cathodes and to take no account of an adjustment to certain and constant cathode potentials, and to exclude a secondary interference of the solvent, for instance by molecular rearrangements. In this general comprehension of the problem it can be said that the well-known chemical rule reoccurs in electrolytical

reduction; viz., in acid solution the formation of aniline is favored, in alkaline solution that of azoxy- and azobenzene.

Löb<sup>1</sup> has tried to explain these facts on the basis of the electrolytic dissociation theory. He emphasizes the fact that in alkaline solution sodium ions, in acid solution hydrogen ions, tend chiefly to effect reduction. In the latter case the possibility of hydrogen addition, which facilitates the formation of hydrazo- and amido-compounds, is present on a large scale. Even if these considerations, particularly the supposition that in alkaline electrolytes the sodium ions form primarily the reducing agent, are thoroughly established, they seem unsuitable as a basis of a general theory of reduction, because Haber has proved by thorough investigations that the typically alkaline reduction products, azoxy- and azobenzene, possess a secondary character, do not belong to the normal course of reaction, but are first formed by the condensations of normal reduction phases. Since Haber has also shown that the primary reduction products in alkaline and acid electrolytes are the same, the divergencies in the results can be explained only by the unequal reaction velocities with which the mentioned condensations occur, so that in this the influence of the sodium ions and hydrogen ions shows itself.

We are indebted to the labors of Bamberger and his pupils<sup>2</sup> and to Haber's<sup>3</sup> extensive investigations for the explanation of the reduction mechanism.

The typical order in alkaline and in acid reduction is: Nitrobenzene  $\rightarrow$  nitrosobenzene  $\rightarrow$  phenylhydroxylamine  $\rightarrow$  aniline. However, further reductions which often interrupt the smooth progress of the process from nitrobenzene to aniline occur between these simple reduction products. A number of possibilities hinder the appearance of the above-mentioned typical reaction scheme unless especial conditions are created; thus

<sup>1</sup> *Ztschr. für Elektrochemie* **3**, 39 (1896).

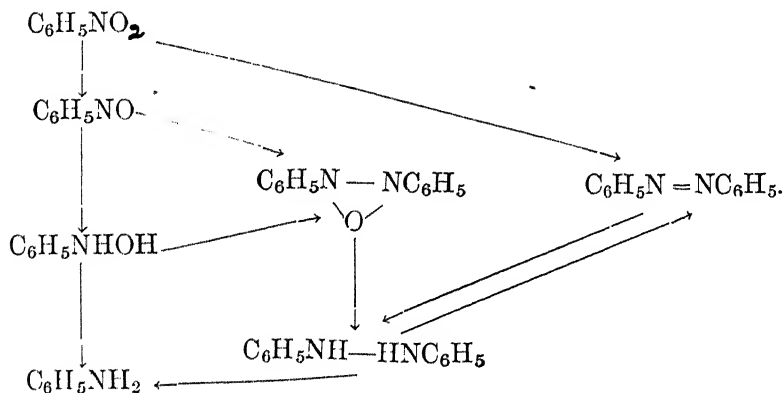
<sup>2</sup> *Ber. d. deutsch. chem. Gesellschaft* **31**, 1500, 1522 (1898); **33**, 274 (1900) et al.

<sup>3</sup> *Ztschr. f. Elektrochemie* **4**, 511 (1898); *Ztschr. f. phys. Chem.* **32**, 271 (1900).

in the first instance the condensation of nitrosobenzene with phenylhydroxylamine to azoxybenzene, which is further reducible to hydrazobenzene; also the reaction of the hydrazobenzene thus produced with unchanged nitro- or nitrosobenzene to azobenzene, which is likewise a primary source of hydrazobenzene; then the rearrangement of the latter to benzidine, that of phenylhydroxylamine to amidophenol or its derivatives, and finally the capability of phenylhydroxylamine to yield azobenzene in alcoholic-alkaline solution with the splitting off of water

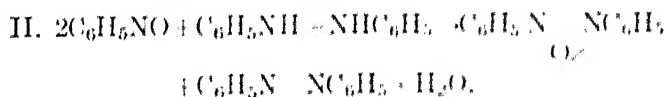
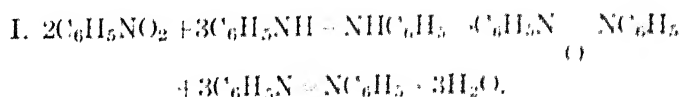
The different processes occur in varying proportions quantitatively or qualitatively, depending upon the nature of the electrolyte and of the cathode material, and upon the current conditions.

The following reduction and reaction scheme can be given in support of Haber's descriptions for the electrolytic processes:

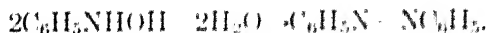


Azoxybenzene is therefore formed by condensation of nitrosobenzene and phenylhydroxylamine. This reaction, like the production of azobenzene, takes place very rapidly under the influence of sodium ions; the ready occurrence of both of these substances in alkaline solution is thus easily explained. Azobenzene is mostly produced by a condensation of nitro-

benzene or nitrosobenzene with hydrazobenzene, which in turn is a direct reduction product of azoxybenzene:



A splitting off of water, especially in alcoholic-alkaline solution, readily converts phenylhydroxylamine into azobenzene:



Azobenzene, like azoxybenzene, can also pass into hydrazobenzene, and further to aniline. In acid solution the molecular rearrangements readily occur: Phenylhydroxylamine to amidophenol, and hydrazobenzene to benzidine and diphenylene. If the problem is to obtain certain reduction phases, the task will be to determine those conditions of experiment which will reduce as far as possible the velocity of all competing reactions. Thus, if we designate all processes which deviate from the straight reduction path nitrobenzene—nitrosobenzene—phenylhydroxylamine—aniline—as secondary condensations and secondary rearrangements, the following conditions will, for example, be presented as suitable for the preparation of aniline: Very high reduction velocity, combined with very low condensation velocity (avoidance of azoxybenzene and azobenzene) and very trifling rearrangement velocity (avoidance of amidophenol).

In like manner the conditions are to be varied according to the object in view: to obtain azoxybenzene the reduction velocity must be lowered, and the condensation velocity increased. The means by which we can accomplish at will this or that reaction will more accurately be explained under the individual reduction phases.

## II. Significance of the Electrical Relations.

It is evident that the whole connection between experimental conditions and the obtainable reduction phase is regulated by the reaction velocities of the competing processes. The possibility of the formation of each reduction product is always present in the reduction of nitrobenzene; only those products, however, can become the principal products which are so rapidly produced that the other possible processes cannot find time to take place to any appreciable extent. Thus only aniline will be principally produced if the immediately occurring phenylhydroxylamine is not rearranged more quickly than the reduction takes place. Inversely, to obtain amidophenol, the rearrangement velocity must be so increased that the reduction velocity of phenylhydroxylamine will be trifling.

The point is to determine the factors upon which the velocity of reaction leading to the separate phases depends.

This question can be divided and simplified. It is, therefore, apparent that a whole series of circumstances must be decisive. The nature of the cathode will regulate the actual reduction speed (p. 11 et seq.), either by furnishing the reducing ions, or by influencing catalytically the reaction between the discharged ions and the depolarizer, or by both influences making themselves felt simultaneously. The concentration of the acid influences the velocity of rearrangement, either of that of the phenylhydroxylamine or of the hydrazobenzene. The nature and concentration of the alkali, and the presence or absence of alcohol, determines the velocity of the condensations or of the splitting off of water from phenylhydroxylamine, and these relations mutually permeate one another. If the problem can thus be subdivided into individual problems, it can also be considerably simplified by the form of the interrogation: Is there *one* factor in which all these relations are decisively expressed; is there *one* quantity which determines clearly the velocities of the possible reactions?

The answer, under certain limitations, is an affirmative



one. The value of the cathode potential wholly includes all single factors—a certain value of the cathode potential corresponds to a wholly certain reduction product, no matter if it occurs primarily or secondarily. To emphasize only the *one* important point—so long as a body acts as a depolarizer it acts codeterminatively on the value of the potential. If its depolarizing property is destroyed by rearrangements, or by condensations which have nothing to do directly with the electrical process, this reaction must express itself in the value of the potential. Of course a certain phase cannot be produced under all conditions, for instance, at optional concentrations of the electrolyte; this shows itself in the fact that it is not then possible to obtain the potential conditioning this phase—the potential always remains the measure for the possible effect. However, these considerations are only true provisionally in the case where the relation in which the potential stands to the current strength and to the concentration of the depolarizer is a permanent one, which can easily be fulfilled by a suitable choice of conditions. Exceptions to the rule and the cause of the exceptions will be explained presently.

Use is not always made of this important fact in practice; the existing chemical experiences, the simplicity of the experiments often render it feasible to produce the desired effect with certainty by observing a series of easily controlled conditions such as concentration, temperature, electrode material, and current density—but these conditions then have only the effect of limiting the potential to the values necessary for obtaining the result. The determination of this relation required some time, and even to-day the connection between potential and reaction velocity is not recognized by all investigators.<sup>1</sup>

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<sup>1</sup> Thus Elbs has recently referred the different behavior of the *o*-, *m*-, and *p*-compounds, in the reduction of the nitrotoluquinolines, to "stereochemical hindrance," laying particular weight on the explanation that the course of the reduction depends upon the cathode potential (Ztschr. f.

Haber<sup>1</sup> deserves the credit of having determined the importance of the potential at unattackable cathodes in the reduction of nitrobenzene. Later Löb and Moore<sup>2</sup> experimentally proved for a whole series of cathode metals and additions that with equal cathode potentials the results are always qualitatively and quantitatively the same; but if the potential is neglected the most varied products result. But the potential is only a measure for the reduction energy if the total current work is essentially employed for the reduction process, and if greater quantities of it are not used up for accomplishing certain other work at the electrodes. Cases in which this occurs have been observed by Russ,<sup>3</sup> and by Haber and Russ.<sup>4</sup> They tried to explain these, as touched upon in the first chapter. It appears, namely, that the electric energy necessary for a certain fixation of the potential of the cathode often depends not only upon the chemical material of the cathode, but also upon its surface and its previous treatment. Retarding or accelerating influences can occur at the electrode; a pre-polarization especially can convert it into an active labile condition, whose cause—perhaps the formation of a gas film absorbed by the electrode—has not yet been explained. If the renewal of such a gas film, or more generally speaking, the restoration of the changeable electrode conditions, demands appreciable quantities of the total work, the potential can no longer serve solely as an expression for the chemical changes at the cathode.

Löb and Moore have experimentally proven the decisive importance of the potential in the reduction of nitrobenzene; the electrodes investigated by them were not seriously affected

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Elektrochemie 10, 579 (1904). In reality it is a question of competitive reaction velocities which must find their expression in the potential.

<sup>1</sup> Ztschr. f. Elektrochemie 4, 511 (1898); Ztschr. f. phys. Chemie 32, 193 (1900).

<sup>2</sup> Ztschr. f. phys. Chemie 47, 418 (1904).

<sup>3</sup> Ibid. 44, 641 (1903).

<sup>4</sup> Ibid. 47, 257 (1904).

by the last-mentioned influences. The results of their investigation are the following:

In the reduction of nitrobenzene in a 2% aqueous sodium-hydroxide solution, according to previous publications, azoxybenzene is formed at platinum and nickel electrodes, azobenzene at lead, tin, and zinc cathodes, and aniline at copper cathodes, especially in the presence of copper powder. It was found that, in an unchangeable experimental arrangement, a cathode potential of 1.8 volts, as measured in connection with the decinormal electrode, could be carried out with all the chosen cathodes and additions. At this constant potential, by using different metals and adding various metallic hydroxides, the whole reduction was carried out and the nature and quantity of the reduction products determined in each case. It turned out that the emphasized differences in the results disappeared and that, with an equal potential of all cathodes, similar yields of azoxybenzene and aniline and traces of azobenzene resulted. The cathodes were of platinum, copper, copper and copper powder, tin, platinum with addition of stannous hydroxide, zinc, platinum with addition of zinc hydroxide, lead, platinum with addition of lead hydroxide, and nickel. The yields of azoxybenzene varied from 41-65%; of aniline 23-53%.

Considering the trifling quantity of the product started with which had to be chosen in order to at all carry out the experiments, and considering the difficulty with which an accurate quantitative separation and determination of the reduction products could be carried out, the proposition that can be laid down as a sure result of the above is that the *cathode potential is the measure for the reduction energy for nitrobenzene when a 2% sodium-hydroxide solution is employed as electrolyte.*

Another investigation may here be mentioned which—chiefly carried out with nitro-bodies—contains ideas which become of general importance and can perhaps furnish a new physicochemical method for determining constitutions.

Panchaud de Bottens<sup>1</sup> has determined the drop in potential

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<sup>1</sup> Ztschr. f. Elektrochemie 8, 305, 332 (1902).

to which a hydrogen electrode is subject on the addition of bodies of the aromatic series. These "depolarizing values," when measured under exactly similar circumstances, are a function of the chemical nature of the depolarizer and are closely related to their composition and constitution. It might be of particular interest to choose an oxygen electrode in place of a hydrogen electrode, since perhaps all organic substances show a depolarizing value when measured by the former. The results are the following:

The depolarization of a hydrogen electrode in the presence of a reducible body was investigated, fifty-three aromatic bodies being thus examined: Nitroso-, nitro- and nitrosamine-, isodiaz- and diazonium-bodies. The investigation of the depolarization was made by taking into consideration its course in time and in connection with the concentration.

1. The reduction energy of hydrogen at platinized platinum electrodes can be given in comparison with reducible bodies as "depolarization value" in volts.

2. Analogously constituted bodies have analogous depolarization values.

3. Different groups of depolarization values correspond to differently constituted groups of bodies.

4. The absolute values of the classes of bodies investigated in acid solution ( $n/1$   $\text{H}_2\text{SO}_4$  or  $n/1$   $\text{CH}_3\text{COOH}$ ) are the following:

- a. Nitroso-compounds = 0.64–0.5 volt,
- b. Mononitro-compounds = 0.33–0.23 volt,
- c. Nitrosamines and isodiazohydrates = 0.16–0.09 volt,
- d. Diazonium compounds = 0.47–0.37 volt,
- e. Isodiazotates, normal diazo-compounds, do not depolarize.

5. Regular laws have not resulted in the case of isomers within a group.

6. In acid solution, in the case of isomers of nitro-disubstitution products, the ortho-position proved to be the one which depolarized the hydrogen electrode the most.

7. The method for the determination of the depolarization value shows in the case of the two investigated isodiazohydrates (isodiazobenzenehydrate and p-nitroisodiazobenzenehydrate) that they belong to the nitrosamines.

### III. Presentation of the Reduction Phases of Nitrobenzene.

An idea of the electrolytic behavior of nitrobenzene is best obtained by the use of the reduction scheme, by carrying out the experiments according to the chief products occurring in the reductions. For after the first observations of Kendall,<sup>1</sup> Elbs,<sup>2</sup> Häussermann,<sup>3</sup> and Löb,<sup>4</sup>—who all taught and showed the variety of obtainable products that it is possible to bring about electrolytically at almost every reduction stage—a desire predominated to find out the conditions which make possible and favor the preponderating formation of a certain substance. The primary reduction products are nitrosobenzene, phenylhydroxylamine and aniline. Secondary substances, i.e. those produced by chemical action, are azoxybenzene and azobenzene, which in turn can give hydrazobenzene or benzidine and aniline. Phenylhydroxylamine can pass into amidophenol and also undergo other rearrangements and condensations. The possibility of causing at will certain phases to yield the chief products of reduction is of great importance for the manufacturing and technical side of the electrolysis of nitrobenzene. The following is known concerning the formation of the separate reduction stages:

**Nitrosobenzene.**—It is natural that so good a depolarizer as nitrosobenzene is at the cathode cannot be separated as such under the conditions of a continuous reduction. Haber,<sup>5</sup> by adding  $\alpha$ -naphthol and hydroxylamine to the electrolyte in alkaline solution, could, however, prove the presence of nitrosobenzene in the form of its characteristic condensation product,

<sup>1</sup> D. R. P. No. 21131 (1883).

<sup>2</sup> Chem. Ztg. 17, 209 (1893).

<sup>3</sup> Ibid., 129, 209 (1893).

<sup>4</sup> Ztschr. f. Elektrochemie 3, 471 (1897).

<sup>5</sup> Ibid. 4, 511 (1898).

benzeneazo- $\alpha$ -naphthol,  $C_6H_5N \cdot NC_{10}H_6OH$ ; similarly in acid solution by adding hydroxylamine and  $\alpha$ -naphthylamine, as benzeneazo- $\alpha$ -naphthylamine,  $C_6H_5N \cdot NC_{10}H_6NH_2$ . These methods of preparation of both dyes are, of course, only of theoretical interest.

**Phenylhydroxylamine.**—Haber<sup>1</sup> electrolyzed a solution of 10 g. nitrobenzene in 215 cc. glacial acetic acid, which was diluted to 425 cc., in an earthenware cylinder, and employed a platinum cathode of 25 sq. cm. surface (one side) and a current density of 1.5, later 1, amp. For this latter a voltage of 80 was at first necessary, on account of the low conductivity of the solution. The temperature was kept below 20° by artificial cooling. After six to eight hours the electrolyte contained large quantities of phenylhydroxylamine. The same investigator<sup>2</sup> in conjunction with Schmidt, on electrolyzing nitrobenzene in alcoholic ammonia with addition of sul-ammoniac, isolated phenylhydroxylamine, besides azoxybenzene and a little azobenzene.

C. F. Boehringer & Söhne and C. Messinger<sup>3</sup> obtain phenylhydroxylamine in a peculiar manner. A lead electrode and an earthenware diaphragm are placed in a container, and a porous carbon cell in the earthenware diaphragm. The lead electrode serves as anode, the carbon cell as cathode. The outer container and the earthenware cell are filled with a 30% sulphuric acid serving as electrolyte; nitrobenzene is forced through the carbon cell towards the earthenware cell under a pressure of 0.5 atmosphere. If the solution is now electrolyzed at a current density of 2 amp. per square decimeter and a temperature up to 25°, phenylhydroxylamine is formed as end-product, since at this low temperature and in the dilute acid no molecular rearrangement into amidophenol can take place.

**Molecular Rearrangement and Condensation Products of Phenylhydroxylamine.**—The difficulty and subtilty of the electrolytic preparation of phenylhydroxylamine depends upon

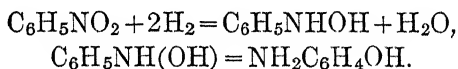
<sup>1</sup> Ztschr. f. Elektrochemie 4, 511 (1898).

<sup>2</sup> Ztschr. f. phys. Chem. 32, 283 (1900).

<sup>3</sup> D. R. P. No. 10905 (1898).

the great reactivity of the body, which reactivity exposes it, even during the electrolysis, to further reactions. In alkaline solution it is chiefly the condensation of phenylhydroxylamine with its predecessor in the reduction, nitrosobenzene, to azoxybenzene; or in alcoholic-alkaline solution the condensation of two molecules to azobenzene. In acid solution the rearrangement phenomena caused by the acids are chiefly important. Owing to the dependence of the rearrangement velocity upon the acid concentration, concentrated acids are best suited for the purpose. The nature of the acid is often decisive for the rearrangement products.

**Amidophenol.**—On reducing nitrobenzene in concentrated sulphuric acid, Noyes and Clement<sup>1</sup> obtained p-amidophenolsulphonic acid. Gattermann and Koppert,<sup>2</sup> by using nitrobenzenesulphonic acid in tolerably concentrated sulphuric acid, got p-amidophenol sulphate. Gattermann,<sup>3</sup> on varying the experimental conditions, also employing concentrated sulphuric acid, obtained para-amidophenol directly from nitrobenzene. He explains the latter's formation by assuming the intermediate production of phenylhydroxylamine, which in further reduction rearranges itself into the end-product.



Some o-amidophenol is formed besides the p-compound.

**Chloraniline.**—Löb<sup>4</sup> has found that p- and o-chloraniline are obtained by the electrolytic reduction of nitrobenzene suspended in fuming hydrochloric acid, nitrobenzene dissolved in alcoholic hydrochloric acid, and nitrobenzene dissolved in mixtures of hydrochloric and acetic acids. With hydrobromic acid the corresponding *bromanilines* are formed.

<sup>1</sup> Ber. d. deutsch. chem. Gesellsch. **26**, 990 (1893).

<sup>2</sup> Chem. Ztg. **17**, 210 (1893).

<sup>3</sup> Ber. d. deutsch. chem. Gesellsch. **26**, 1844 (1893).

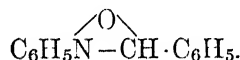
<sup>4</sup> Ztschr. f. Elektrochemie **3**, 46 (1896); Ber. d. deutsch. chem. Gesellsch. **29**, 1894 (1896).

The reaction takes place as shown in the following equations:

1.  $\text{C}_6\text{H}_5\text{NO}_2 + 4\text{H} = \text{C}_6\text{H}_5\text{NHOH} + \text{H}_2\text{O}.$
2.  $\text{C}_6\text{H}_5\text{NHOH} + \text{HCl} = \text{C}_6\text{H}_5\text{NHCl} + \text{H}_2\text{O}.$
3.  $\text{C}_6\text{H}_5\text{NHCl} = \begin{matrix} \text{O}^- \\ \text{p}^- \end{matrix} \text{ClC}_6\text{H}_4\text{NH}_2.$

The phenylchloramine formed by the action of hydrochloric acid on phenylhydroxylamine changes by molecular rearrangement into o- and p-chloraniline.

**Condensation Products with Aldehydes.**—Gattermann<sup>1</sup> has obtained direct proof of the intermediate formation of phenylhydroxylamine in the preparation of amidophenol by adding benzaldehyde to the solution at the beginning of the electrolysis. He was thus able to isolate a condensation product of phenylhydroxylamine with benzaldehyde. In this way he obtained from nitrobenzene *benzylidene-phenylhydroxylamine*,



The presence of formaldehyde in the electrolytic reduction of nitro-compounds produces an effect entirely different from that caused by the addition of benzaldehyde. The phenomena occurring in this case have been thoroughly investigated by Löb.<sup>2</sup>

The fundamental object of his researches differs from that of Gattermann, in that Löb undertakes to establish the separate phases of the reduction of the nitro-group. This he accomplishes by the addition of formaldehyde to the electrolyte under varying conditions, and as a result the intermediate products, at the moment of their formation, combine with formaldehyde, producing condensation compounds which do not undergo further decomposition. By regulating the potential or density of the current the reaction can at

<sup>1</sup> Ber. d. deutsch. chem. Gesellsch. 29, 3040 (1896).

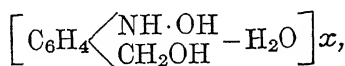
<sup>2</sup> Ztschr. f. Elektrochemie 4, 428 (1898).



will be checked at a perfectly definite phase of reaction.

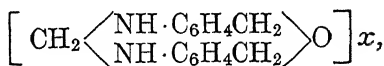
In the electrolysis of nitrobenzene by this method, the following products were formed:

1. *p*-Anhydrohydroxylaminebenzyl alcohol,



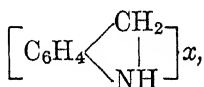
which may also be directly prepared by the action of formaldehyde on phenylhydroxylamine.

2. Methylenedi-*p*-anhydroamidobenzyl alcohol,



a reaction product of formaldehyde and aniline.

3. Anhydro-*p*-amidobenzyl alcohol,<sup>1</sup>



which can be likewise obtained by the action of formaldehyde upon aniline.

**Azoxybenzene.**—This substance was recognized first in 1893 in the investigations of Elbs,<sup>2</sup> Häussermann,<sup>3</sup> and Scherer as one of the reduction products occurring both in acidic and alkaline electrolytic reduction of nitrobenzene. Berger and Haber then explained its formation by the condensation of phenylhydroxylamine and nitrosobenzene by electrolyzing nitrobenzene suspended in dilute alkaline or alkaline-salt solutions at unattackable potentials.

<sup>1</sup> Ber. d. deutsch. chem. Gesellsch. **31**, 2037 (1898).

<sup>2</sup> Chem. Ztg. **17**, 209 (1893).

<sup>3</sup> Ibid., 129 (1893).

<sup>4</sup> D. R. P. No. 79731 (1894).

<sup>5</sup> Ztschr. f. Elektrochemie **7**, 335 (1900); Ztschr. f. phys. Chem. **6** (1900).

(platinum, nickel, mercury), succeeded in finding a method which gives a good material- and current-yield of azoxybenzene almost free from other reduction products. In this case the unattackable cathode plays a leading part, aside from the use of aqueous electrolytes. The choice of attackable cathodes modifies the process very considerably, the nature of the metal producing individual effects.

**Azobenzene.** — Alcoholic-alkaline solutions act differently from aqueous-alkaline electrolytes. Even if unattackable electrodes are employed with the former, the process can be regulated so as to give very good yields of azobenzene. This was demonstrated by Elbs and Kopp.<sup>1</sup> Two concurrent processes determine presumably the azobenzene formation, firstly, the splitting off of water from two molecules of phenyl-hydroxylamine produced by the influence of the alcoholic-alkaline solution; secondly, the reaction of hydrazobenzene (resulting from the azoxybenzene formed secondarily) with unchanged nitrobenzene or nitrosobenzene. That the latter reaction occurs is shown by the fact that, if the electrolysis is prematurely interrupted, azoxybenzene and azobenzene and hydrazobenzene are always present. When alcoholic electrolytes were employed it proved advantageous to substitute for the free alkali sodium acetate which, on account of its easy solubility in alcohol, its good conductivity and trifling action on the diaphragm, possesses considerable advantages over sodium hydroxide. These processes are not technically valuable on account of the employment of alcohol.

Bayer & Co.<sup>2</sup> seek to avoid this latter inconvenience by reducing nitrobenzene, suspended in aqueous alkaline or alkali-salt solutions, in the presence of such metallic cathodes, or the addition of such metallic salts, whose oxides are soluble in caustic alkali,—for instance lead, zinc, tin, or their salts. The yields of azobenzene obtained by this method are said to be

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<sup>1</sup> Ztschr. f. Elektrochemie 5, 108 (1898); D. R. P. No. 100233, 100234 (1898).

<sup>2</sup> D. R. P. No. 121899 and 121900 (1899).

almost quantitative. According to a patent<sup>1</sup> of the Farbwerke vorm. Meister, Lucius & Brünig, the reduction of nitrobenzene to azobenzene can also be accomplished in aqueous-alkaline solution, if the electrolysis is carried out without a diaphragm but with a large cathode and small anode and at a high temperature (105°–115°).

**Hydrazobenzene.** In hydrazobenzene we have a reduction product of nitrobenzene which is next in importance to aniline, being employed in large quantities in the manufacture of benzidine. Its electrolytic preparation exceeds in importance that of aniline; the purely chemical method of preparing benzidine is more complicated, less smooth, and gives poorer yields than that of aniline, so that great exertions have been put forth to make the electrolytic manufacture of the former practical. According to Straub,<sup>2</sup> hydrazobenzene is obtained from nitrobenzene in alcoholic-alkaline solution by choosing such suitable conditions of solution that all intermediate products are kept in solution, but the difficultly soluble hydrazobenzene is precipitated, thus withdrawing it from the further action of the current.

Both azoxybenzene and azobenzene are converted, by suitable reduction, into hydrazobenzene. Both methods have already been followed. Ellis and Kopp<sup>3</sup> work in alcoholic-alkaline solution and obtain hydrazobenzene from nitrobenzene in one process, by way of azoxy- and azobenzene. They obtain excellent yields, but by means of the technically impractical alcohol method. Bayer & Co. can make use of their patented process<sup>4</sup> for the preparation of azobenzene in the making of hydrazobenzene, by continuing the electrical reduction, and obtain good yields of this latter substance.

Löb chooses azoxybenzene as the primary substance in making hydrazobenzene. This method corresponds to the theoretically demanded reduction course, as explained for the azoxybenzene and azobenzene formation. According to this

<sup>1</sup> D. R. P. No. 141535 (1902).

<sup>2</sup> D. R. P. No. 79731 (1894).

<sup>3</sup> *Ztschr. f. Elektrochemie* 5, 108 (1898).

<sup>4</sup> See p. 159.

theory azobenzene is a condensation product of hydrazobenzene and nitro- or nitrosobenzene.

**Benzidine.**—That nitrobenzene, by electrolytical reduction in acid solution, can directly yield benzidine, was first proved by Häussermann,<sup>1</sup> who used sulphuric acid. Löb<sup>2</sup> later proved the same to be true for hydrochloric-, acetic-, and formic-acid electrolytes. However, several reactions predominate in this direct acid reduction, which prevent the carrying out of the reaction up to hydrazobenzene, or the formation of benzidine. Phenylhydroxylamine may particularly be mentioned in this connection. In alcoholic-acid solution it is partly rearranged to amidophenol or its ethers, and partly reduced to aniline. Azoxybenzene, in acid solution, is the starting-point in the benzidine formation; however, in this case, the combining velocity of nitrosobenzene and phenylhydroxylamine is not very great, so that the latter is to a very considerable extent subject to the more rapidly acting influence of the acid.

Besides azoxybenzene, azobenzene also gives hydrazobenzene, as already mentioned, e.g. in acid solution benzidine results. Azobenzene, however, is formed only in very small quantity.

Löb,<sup>3</sup> convinced of the futility of thus being able to obtain a good yield of benzidine by a direct reduction of nitrobenzene in acid solution, sought to carry out the benzidine process by a careful realization of the conditions theoretically required—primary preparation of azoxy- or azobenzene in the best quantitative yields, i.e. in electrolytes, containing alkali or alkali-salt, then reducing these products in acid solution. Two processes thus resulted. In the first one the electrolytic reduction was carried out to azobenzene in alcoholic-alkaline solution, then the cathode solution was acidified with sulphuric acid, and the further reduction and molecular rearrangement combined in one operation. The second process, which was

<sup>1</sup> Chem. Ztg. 77, 108 (1893).

<sup>2</sup> Ztschr. f. Elektrochemie 3, 471 (1897); Ber. d. deutsch. chem. Gesellsch. 29, 1894 (1896).

<sup>3</sup> Ztschr. f. Elektrochemie 7, 320, 333, 597 (1900–1901).

worked out after the discovery of the electrolytic preparation of azoxybenzene, avoids the objection of adding alcohol, and takes place primarily in aqueous alkali or alkali salt solution at unattackable cathodes with azoxybenzene as the result. It appears that azoxybenzene, in sulphuric acid solution, is an extremely poor depolarizer, but that the further reduction takes place very readily in a hydrochloric acid electrolyte with the addition of a trifling quantity of stannous chloride. Some diphenylene and aniline is always formed besides the benzidine, the aniline probably by a splitting up and reduction of hydrazobenzene before its rearrangement.

**Aniline.** The reactions which stand in the way of the benzidine preparation are also of a disturbing nature in the preparation of aniline by reduction in acid solution; especially the reactivity of the phenylhydroxylamine, its molecular rearrangement and condensation, at first hindered the quantitative further reduction to aniline. The overcoming of these obstacles was brought about by the choice of suitable cathode metals. Ellis first observed the influence of the cathode metal in the electrolytic preparation of aniline. Löb later made the same observation. Ellis<sup>1</sup> found that the replacement of the platinum cathode by one of zinc considerably favored the formation of aniline from nitrobenzene in acid solution; later<sup>2</sup> he obtained with Sillermann the same successful result when any kind of a cathode was used with the addition of a zinc salt. The same investigators have also proved in previous researches<sup>3</sup> that, under similar circumstances, and in sulphuric acid solution, much more aniline besides amidophenol, is produced at a lead cathode than at a platinum cathode.

Löb,<sup>4</sup> independently of these observations, found that an almost quantitative yield of aniline can be obtained from nitrobenzene in hydrochloric acid solution and at a lead cathode;

<sup>1</sup> Chem. Ztg. 17, 209 (1893).

<sup>2</sup> Ztschr. f. Elektrochemie 7, 589 (1901).

<sup>3</sup> Ibid. 3, 472 (1896).

<sup>4</sup> Ibid. 4, 430 (1898).

later Elbs and Silbermann<sup>1</sup> also obtained 90 per cent of the theoretical yield of aniline with the aid of a lead cathode.

We are indebted to C. F. Boehringer & Söhne<sup>2</sup> for the comprehensive exploitation of the influence of cathode material in the preparation of aniline. They have patented the results of their experiments. The importance of the decisive conditions of the experiments, as in those of Elbs and Silbermann and of Löb, lies in the increase of the reduction velocity of phenylhydroxylamine to aniline, so that competing rearrangement and condensation reactions are given no time to occur. Almost quantitative yields of aniline are obtained. The nature of the process consists in reducing the nitrobenzene in acid solution, or suspension, by means of indifferent electrodes and with the addition of a tin, copper, iron, chromium, lead, or mercury salt, or the corresponding metal in a finely divided state.

The metal employed, or the corresponding degree of quantivalence of the metal ion, is regenerated by the current, depending upon the greater or less electrolytic ismotic pressure of the metal. Cathodes of tin can also be employed instead of the tin salt.

It may be mentioned incidentally, that according to investigations by Möller<sup>3</sup> a strong odor of phenylisocyanide,  $C_6H_5N=C$ , occurs in the electrolysis of nitrobenzene in alcoholic-alkaline solution and without a diaphragm. But a separation of the carbylamine could not be made. Homologues of nitrobenzene, when electrolyzed under analogous conditions, also yield isonitrile.

### *c. Substitution Products of Nitrobenzene.*

#### **I. General Laws governing Substitution.**

The reduction scheme sketched by Haber for the reduction of nitrobenzene also holds true for the substitution products of nitrobenzene in so far as the formation of their reduction phases can be coordinated to the same reduction, condensation, or molecular rearrangement processes. But the decisive influ-

<sup>1</sup> Ztschr. f. Elektrochemie 7, 589 (1901).

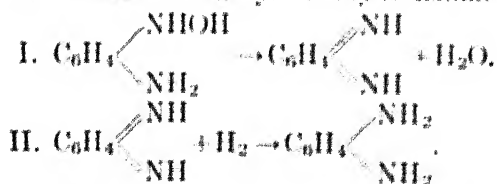
<sup>2</sup> D. R. P. No. 116942 (1899); 117007 (1900).

<sup>3</sup> Ztschr. f. Elektrochemie 5, 463 (1898).

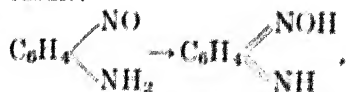
ence of the substituents manifests itself in various ways. In the first place, the experimental conditions determined for the preparation of certain reduction stages of nitrobenzene do not obtain for its derivatives, at least only in a limited manner. The position and nature of the substituents also often hinder the preparation of single phases. In other words: the reaction velocity with which reduction, condensation, and rearrangement take place is fundamentally influenced.

Nevertheless some reactions are known which possess a certain general applicability. This is true of Gattermann's reduction in concentrated sulphuric acid, which give mostly amidophenols, if the ortho- or para-position is unoccupied. Only p-nitrotoluene and the nitroaldehydes form exceptions, which will be discussed.

The reduction in alkaline solution likewise leads almost always to azo- and azoxy-bodies, or hydrazo-bodies. The laws here predominating have chiefly been investigated by Ellis<sup>1</sup> and his pupils. The exceptions to the rule, the occurrence of amines in place of azo- and azoxy-compounds were clearly explained by Ellis. p-Nitraniline, electrolyzed under the same conditions which give m-diamidobenzene from m-nitraniline, yields only p-phenylenediamine. This phenomenon is based on the fact that p-nitraniline readily yields quinone derivatives, but m-nitraniline does not. Thus the primarily produced p-amidophenylhydroxylamine is changed to quinonediazide, which on further reduction can yield only a diamine:



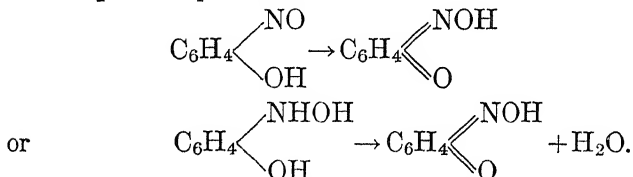
Or this rearrangement occurs already in the nitroso-phase, which leads to the same result:



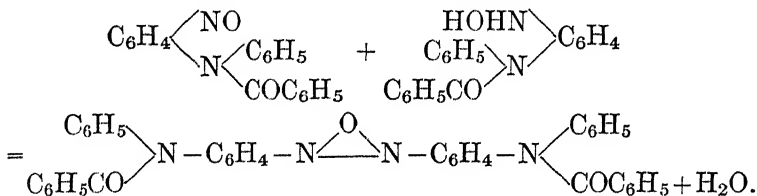
<sup>1</sup> Ztschr. f. Elektrochemie 7, 133, 141 (1900).

Since the tendency to form quinone derivatives is lacking in m-nitraniline, the nitroso- and hydroxylamine phase can unite normally to the azo-body.

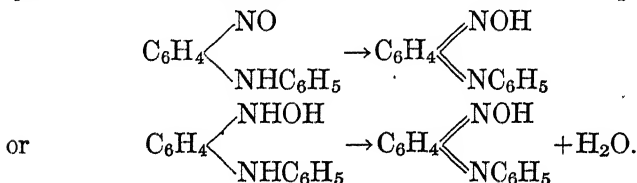
For the same reason perhaps the exclusive formation of o- and p-amidophenol occurs:



These quinone derivatives, by further reduction, can produce only amidophenols. If the quinone formation is prevented from taking place, for instance by esterifying the hydroxyl-group, the normal reaction to azoxy-bodies occurs. o- and p-Nitroanisole pass smoothly into azoxy- or azo-derivatives. The acylizing of the amido-group in the case of o- and p-nitroamines hinders likewise the quinone, and therewith the amine, formation. The azoxy-body is smoothly formed, thus:



But the alkylation does not prevent the formation of quinone and therefore the reduction to the amido-phase:



Elbs sums up in the following manner the rules which apply to the electrochemical reduction of aromatic mononitro-bodies in alkaline solution. Hereby it must be taken into consideration that the primarily formed azoxy-body, under the conditions chosen by Elbs, leads to the azo-body.



1. Nitrobenzene and its homologues give azo-bodies; amines do not occur, or only in traces.

2. Halogenized nitrobenzenes and their homologues yield azo-compounds; difficulties occasionally occurring are caused by the alkaline cathode fluid attacking the halogen made mobile by the nitro-group, or inversely the nitro-group made mobile by several halogen atoms.

3. Nitrobenzene-m-sulphonic acid and its homologues give azo-bodies.

4. Nitrobenzenecarboxylic acids yield azo-compounds, but only the o-acids behave differently.<sup>1</sup>

5. m- and p-Nitroacid-nitriles yield azo-bodies, with or without a partial saponification, depending upon the conditions of the experiment.

6. m-Nitraniline and its homologues give azo-bodies, but o- and p-nitraniline and its homologues, on the contrary, give diamines.

The same rule obtains for the secondary and tertiary amines derived from the three nitranilines.

7. Acylized nitranilines (acidnitroamides) and their homologues give azo-bodies, no matter which position the nitro-group occupies in regard to the acylized amido-group. The cathode fluid must be kept approximately neutral during reduction, otherwise the acid amides are saponified if the solution becomes considerably alkaline.

8. o- and p-Nitrophenols give amidophenols.

9. Nitrophenol ethers give azo-bodies, no matter what position the nitro-group occupies.

These rules do not hold true for dinitro-bodies.

The experiences gained in the electrolysis of nitrobenzene concerning the influences of the cathode material have also obtained in great measure, with the substituted nitrohydrocarbons. The general result can be summed up in the statement that at unattackable cathodes, such as platinum, nickel,

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<sup>1</sup> Löb, *Ztschr. f. Elektrochemie* 2, 532 (1896).

and mercury, in aqueous-alkaline solution azoxy-bodies<sup>1</sup> are produced, and at attackable cathodes, such as lead or copper, azo-, hydrazo-,<sup>2</sup> and even amido-compounds are formed. The latter are obtained by the method of C. F. Böhringer & Söhne,<sup>3</sup> using a copper cathode, or an unattackable cathode with addition of copper powder. o-Toluidine, m-phenylenediamine from m-nitraniline, and  $\alpha$ -naphthylamine, in addition to aniline, were prepared in good yields by this method.

In alcoholic solution this difference does not occur so distinctly; it is also easy to reduce to the hydrazo-phase at unattackable electrodes.

The influence of the cathode metal is much more manifest when acid electrolytes are employed than in alkaline reduction. In alkaline solution at copper electrodes, if we except the last-mentioned process, the rapidly occurring condensation of the first reduction phases—of the nitroso- and hydroxylamine body—always leads immediately to the azoxy-body and makes this appear to be the typical product of the alkaline reduction, which can in turn be further reduced. In acid solution this condensation takes place so slowly that the molecular rearrangement of the hydroxylamine and its further reduction to amine has time to take place alongside the formation of the azoxy-body and the reduction of the latter to the hydrazo-compound or benzidine.<sup>4</sup>

The increased reactivity of the whole molecule or single groups, which is often associated with the entrance of nitro-groups, is also apparent in the capability of some nitro-bodies to be relatively easily oxidized. The little that is known is appended to the description of the behavior of the individual members. The characteristic features of the oxidation processes in question have been explained in the first chapter (p. 27 et seq.).

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<sup>1</sup> Ztschr. f. Elektrochemie 7, 335 (1900).

<sup>2</sup> D. R. P. No. 121899 and 121900 (1899).

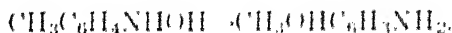
<sup>3</sup> D. R. P. No. 130742 (1901).

<sup>4</sup> Cf. Häussermann, Chem. Ztg. 17, 209 (1893).

## II. Homologues of Nitrobenzene.

## NITROTOLUENES

**o-Nitrotoluene** behaves very much like nitrobenzene. It gives *o*-tolidine and a little *o*-toluidine in sulphuric- or hydrochloric-acid solution (Haussermann).<sup>1</sup> In concentrated sulphuric acid Gattermann and Abresch<sup>2</sup> obtained *o*-amido-*m*-cresol:



Benzylidene-*o*-tolylhydroxylamine,<sup>3</sup> corresponding to the benzylidenephénylhydroxylamine, is produced in the presence of benzaldehyde.

According to the experiments of Haussermann,<sup>4</sup> Ellis and Kopp,<sup>5</sup> and Löb,<sup>6</sup> azotoluene is primarily and almost exclusively produced in alkaline-alcoholic solution, and, on further reduction, hydrazotoluene. The same results can also be obtained as shown in the process of the above-mentioned patents for the preparation of azo- and hydrazobenzene. If electrolyzed in alkaline-aqueous suspension, there is formed on the contrary, azoxytoluene (process of Löb<sup>7</sup>), which can be converted into *o*-tolidine in a hydrochloric-acid electrolyte with tin cathodes, or at an unattackable cathode with additions of stannous chloride.

A solution of *o*-nitrotoluene in a mixture of sulphuric and acetic acids, if oxidized at a platinum anode, gives a poor yield (about 30 per cent.) of *o*-nitrobenzyl alcohol (Pierron<sup>8</sup>).

**m-Nitrotoluene**, if electrolyzed in concentrated sulphuric acid, passes into *m*-amido-*o*-cresol (Gattermann and Heider<sup>9</sup>). If benzaldehyde is present, benzylidene-*m*-tolylhydroxylamine forms (Gattermann<sup>10</sup>).

<sup>1</sup> Chem. Ztg. 17, 209 (1893).

<sup>2</sup> Ber. d. deutsch. chem. Gesellsch. 27, 1929 (1894).

<sup>3</sup> Ibid. 29, 3040 (1896).

<sup>4</sup> Chem. Ztg. 17, 129 (1893).

<sup>5</sup> Ztschr. f. Elektrochemie 5, 110 (1899).

<sup>6</sup> Ibid. 5, 459 (1899).

<sup>7</sup> Ibid. 7, 335 (1900).

<sup>8</sup> Bull. Soc. Chim. [3] 25, 852 (1901).

<sup>9</sup> Ber. d. deutsch. chem. Gesellsch. 27, 1930 (1894).

<sup>10</sup> Ibid. 29, 3040 (1896).

Electrolyzed in alcoholic-alkaline solution, according to the directions of Ellbs, *m*-azotoluene is almost quantitatively produced; the further current action gives *m*-hydrazotoluene (Rohde<sup>1</sup>).

Löb and Schmitt<sup>2</sup> electrolyzed *m*-nitrotoluene in alkaline-aqueous suspension, employing various cathode metals in order to determine their influence. The other conditions of the experiments were the same. *m*-Azoxytoluene, which is to a small extent converted into hydrazotoluene, and *m*-toluidine are produced. The yields vary, depending upon the nature of the cathode: the reduction was weakest at nickel cathodes, i.e., it hardly passed beyond the azoxy-phase; at zinc, copper, and copper in the presence of copper powder, the yield of amine increases in the given series of the metals, while that of azoxytoluene decreases. The following table shows these relations. Five grams *m*-nitrotoluene gave:

Electrode,	Yield in Grams of		
	Azoxytoluene,	Hydrazotoluene	Toluidine,
Nickel, . . . . .	2.47	0.36	0.46
Zinc, . . . . .	2.42	0.29	0.56
Copper, . . . . .	1.83	0.24	1.16
Copper and copper powder	1.38	0.17	1.68

Pierron,<sup>3</sup> by oxidizing electrolytically *m*-nitrotoluene under the conditions chosen for the *o*-nitrotoluene, obtained about 20 per cent *m*-nitrobenzaldehyde.

***p*-Nitrotoluene.**—In dilute sulphuric-acid solution, Häussermann<sup>4</sup> obtained *p*-toluidine as the chief product; Gattermann and Koppert,<sup>5</sup> by reducing in concentrated sulphuric

<sup>1</sup> Ztschr. f. Elektrochemie **5**, 322 (1899).

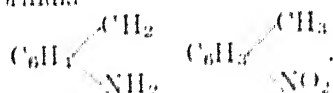
<sup>2</sup> Ibid. **10**, 756 (1904).

<sup>3</sup> Bull. soc. chim. [3] **25**, 852 (1901).

<sup>4</sup> Chem. Ztg. **17**, 209 (1893).

<sup>5</sup> Ber. d. deutsch. chem. Gesellsch. **26**, 1852, 2810 (1893); D. R. P. No. 75261 (1893).

acid, found a process varying from the normal reaction, since the amidophenol formation cannot occur when the p-position is occupied. The reduction leads to nitroamido-o-benzyl alcohol, a substance evidently produced by condensation of the intermediately occurring p-amidobenzyl alcohol with nitrotoluene and having the formula



On further electrolytic reduction this compound is converted into diamidophenyltolylmethane.

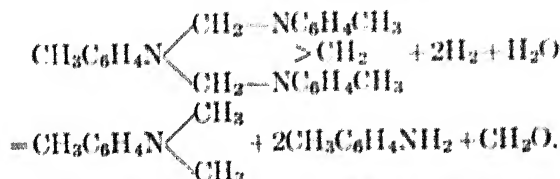
If benzaldehyde is added to the sulphuric acid, benzylidene-p-tolylhydroxylamine is normally produced (Gattermann<sup>1</sup>).

C. F. Boehringer & Söhne<sup>2</sup> found that, if cathodes of tin, copper, lead, iron, chromium, or mercury are chosen, or the salts of these metals at unattackable cathodes are added to the electrolytes, p-nitrotoluene in a hydrochloric-acid electrolyte is smoothly converted into p-toluidine.

Löb<sup>3</sup> found that, if p-nitrotoluene, in alcoholic-hydrochloric acid solution or aqueous-hydrochloric acid suspension, is electrolytically reduced, preferably at lead cathodes in the presence of formaldehyde, there are formed p-dimethyltoluidine and a condensation product of p-toluidine and formaldehyde. According to Goecke,<sup>4</sup> this has the composition



and possesses perhaps the constitution of a trimethylenetritoluidine, which, on further reduction, yields p-dimethyltoluidine:



<sup>1</sup> Ber. d. deutsch. chem. Gesellsch. **29**, 3040 (1896).

<sup>2</sup> D. R. P. No. 116942 (1899); 117007 (1900).

<sup>3</sup> Ztschr. f. Elektrochemie **4**, 428 (1898).

<sup>4</sup> Ibid. **9**, 470, (1903).

The excess of formaldehyde present in the liquid again acts on the toluidine, so that a mixture of dimethyltoluidine and trimethylenetritoluidine results.

In alcoholic-alkaline solution Ellbs,<sup>1</sup> Ellbs and Kopp,<sup>2</sup> and Löb<sup>3</sup> obtained p-azotoluene. If the electrolysis is prematurely interrupted, the electrolyte contains large quantities of p-azoxytoluene; on prolonged electrolysis p-hydrazotoluene is quantitatively produced, according to the process of Ellbs.

Löb and Schmitt<sup>4</sup> investigated the behavior of p-nitrotoluene in alkaline-aqueous suspension at different cathodes. The result is similar to that obtained in the case of m-nitrotoluene, but the azoxy-body was always contaminated with some azo-compound. Five grams p-nitrotoluene gave the following:

Electrode.	Yield in Grams of		
	Azotoluene Azoxytoluene	Hydrazo- toluene.	Toluidine.
Nickel . . . . .	2.66	0.19	0.67
Zinc . . . . .	2.52	0.15	0.88
Copper . . . . .	2.10	0.11	1.31
Copper and copper powder .	1.70	0.05	1.89

If the current yields obtained under similar conditions from m- and p-nitrotoluene are compared with one another, it is found that the p-compound is more easily reducible than the m-body. The influence of the position of the methyl group is thus shown both in the chemical result and the resistance towards reducing agents.

Ellbs,<sup>5</sup> by electrolytically oxidizing p-nitrotoluene in a mixture of concentrated acetic and sulphuric acids at a large platinum anode, obtained p-nitrobenzyl alcohol,—current yield 30 per cent, material yield 40 per cent.

<sup>1</sup> Chem. Ztg. 17, 209 (1893); Ztschr. f. Elektrochemie, 4, 499 (1898).

<sup>2</sup> Ztschr. f. Elektrochemie 5, 110 (1898).

<sup>3</sup> Ibid. 5, 459 (1899).

<sup>4</sup> Ibid. 10, 756 (1904).

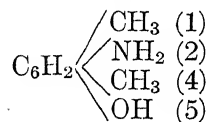
<sup>5</sup> Ibid. 2, 522 (1896).

If the electrolysis is carried out in 80% sulphuric acid, both *p*-nitrobenzaldehyde and the alcohol are obtained (Labhardt and Zschoche<sup>1</sup>).

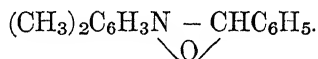
C. F. Boehringer & Söhne<sup>2</sup> add 0.1 part by weight per litre of manganese sulphate to the anode electrolyte,—a mixture of sulphuric and acetic acids,—and obtain smoothly *p*-nitrobenzoic acid at a lead-peroxide anode.

#### NITROXYLENES.

**Nitro-*p*-xylene**, reduced in concentrated sulphuric acid, gives the corresponding amidoxymenol (Gattermann and Heider<sup>3</sup>):



Gattermann,<sup>4</sup> by adding benzaldehyde during the reduction, obtained the benzylidene-derivative



***p*-Nitro-*o*-xylene** was reduced by Elbs and Kopp<sup>5</sup> in alcoholic alkaline solution with addition of sodium acetate. They obtained good yields of azoxy-, azo- and hydrazoxylenes.

***p*-Nitro-*m*-xylene**, when treated similarly gives analogous products.<sup>6</sup>

Elbs and his pupils<sup>6</sup> obtained in the same manner the corresponding azoxy-, azo- and hydrazo-bodies from *o*-nitrobenzylaniline, *p*-nitrobenzylaniline, nitrotolylaminophenylmethane,  $\text{NH}_2\text{C}_6\text{H}_4\text{CH}_2\cdot\text{C}_6\text{H}_3\text{CH}_3\text{NO}_2$ , and *m*-nitroleucomalachite green  $[(\text{CH}_3)_2\text{NC}_6\text{H}_4]_2\text{CH}\cdot\text{C}_6\text{H}_4\text{NO}_2$ ; but the last-mentioned substance was not reduced to the azo-phase.

<sup>1</sup> Ztschr. f. Elektrochemie 8, 93 (1902).

<sup>2</sup> D. R. P. No. 117129 (1900).

<sup>3</sup> Ber. d. deutsch. chem. Gesellsch. 27, 1930 (1894).

<sup>4</sup> Ibid. 29, 3040 (1896).

<sup>5</sup> Ztschr. f. Elektrochemie 5, 110 (1898).

<sup>6</sup> Ibid. 7, 136 (1900).

**m-Dinitrobenzene**, on reduction in concentrated sulphuric acid, is converted into o-p-diamidophenol (Gattermann and Abresch<sup>1</sup>).

**o-p-Dinitrotoluene** (2.4) is analogously reduced to 2.4.5-diamidocresol. Sachs and Kempf<sup>2</sup> oxidized this substance electrolytically in sulphuric acid solution at a lead anode and obtained a medium yield dinitrobenzoic acid.

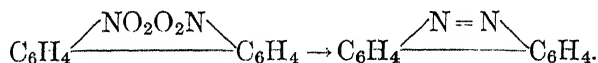
**2.4.6-Trinitrotoluene** gives analogously trinitrobenzoic acid.

**p-Dinitrostilbene**. While carrying out some experiments on the dye "sun yellow," which is obtained by warming p-nitrotoluenesulphonic acid with sodium hydroxide, Elbs and Kre-  
mann<sup>3</sup> worked on the electrochemical reduction of several stilbene derivatives.

They obtained the following results: *p*-Dinitrostilbene, reduced in alkaline solution, gives p-azoxystilbene; in hydrochloric-acid solution with addition of stannous chloride (method of C. F. Boehringer & Söhne), p-diaminostilbene.

**o-Nitrodiphenyl** and *p*-nitrodiphenyl in alkaline electrolytes give the azoxy-derivatives (Elbs); p-nitrodiphenyl also gives inconsiderable quantities of p-amidodiphenyl, while in alcoholic-sulphuric acid at platinum and lead cathodes it is easily reduced to p-amidodiphenyl (Fichte and Sulzberger<sup>4</sup>).

**2.2-Dinitrodiphenyl** was reduced by Wohlfahrt,<sup>5</sup> in accordance with Elb's process, and gave a very good yield of phenazone, while in hydrochloric-acid electrolyte with the addition of stannous chloride hydrophenazone hydrochloride was formed.



The method of Wohlfahrt has been extended by Ullmann and Dieterle<sup>6</sup> to several o-dinitrodiphenyl derivatives. The

<sup>1</sup> Ber. d. deutsch. chem. Gesellsch. **26**, 1848 (1893).

<sup>2</sup> Ibid. **35**, 2712 (1902).

<sup>3</sup> Ztschr. f. Elektrochemie **9**, 416 (1903).

<sup>4</sup> Ber. d. deutsch. chem. Gesellsch. **37**, 881 (1904).

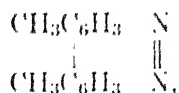
<sup>5</sup> Journ. f. prakt. Chem. [2] **65**, 295 (1902).

<sup>6</sup> Ber. d. deutsch. chem. Gesellsch. **37**, 23 (1904).

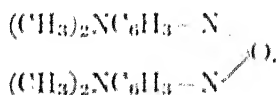


corresponding phenazones are formed in alcoholic-alkaline electrolytes.

2·2-Dinitro-4·4-ditolyl gives the 3·8-dimethylphenazone,

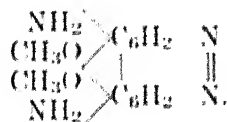


2·2-Dinitrobenzidine gives the 3·8-Diaminophenazone, and *Dinitrotetramethyldiaminodiphenyl* the 3·8-tetramethyldiaminophenazone. This substance is also produced in the electric reduction of tetramethyldiaminophenazone oxide



Dinitrotetraethyldiaminodiphenyl gives the 3·8-tetraethyl-diaminophenazone,

Dinitroanisidine, the 3·8-diaminodimethoxyphenazone



### III. Halogen Derivatives of Mononitro-bodies.

These behave quite analogously to the nitro-compounds containing no halogens. According to the process of Elbs,<sup>1</sup> if these substances are reduced in alcoholic-alkaline solution, there result azoxy-, azo- and hydrazo-bodies. The difficulties caused by the increased activity of the nitro-group and the attackability of the halogen have already been mentioned under the discussion of the general laws. The following substances have been investigated in this manner:

**o-Chlornitrobenzene** (by-products: o-chloraniline and o-aminodiphenol), **m-chlornitrobenzene**, **p-chlornitrobenzene**, **p-dichlor-**

<sup>1</sup> Ztschr. f. Elektrochemie 7, 136 (1900).

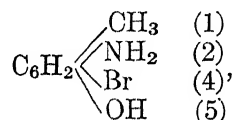
(2,5)nitrobenzene (by-products: p-dichloraniline and chloraminophenol ( $\text{ClOHC}_6\text{H}_3\text{NH}_2$ ), o-bromnitrobenzene, m-bromnitrobenzene, p-bromnitrobenzene, m-iodonitrobenzene, p-iodonitrobenzene, o-chlor-m-nitrotoluene (by-products: o-chlor-m-toluidine), o-chlor-p-nitrotoluene, p-chlor-o-nitrotoluene, p-chlor-m-nitrotoluene (by-products: o-chlor-m-toluidine and o-amino-m-cresol).

Gattermann's reaction also proceeds smoothly with the halogen derivatives, if the para-position to the nitro-group is not occupied.

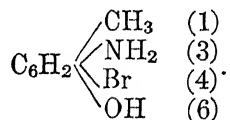
p-Chlornitrobenzene, on account of the mobility of its chlorine atom, is converted in concentrated sulphuric acid into p-amidophenol (Noyes and Dorrance<sup>1</sup>).

m-Bromnitrobenzene gave a good yield of bromamidophenol (Gattermann and Heider<sup>2</sup>).

p-Brom-o-nitrotoluene gives the bromamidocresol.



p-Brom-m-nitrotoluene yields analogously the bromamidocresol.



#### IV. Nitrophenols.

o-Nitrophenol, reduced electrolytically, gives a good yield of o-amidophenol both in alkaline-aqueous solution at platinum cathodes (Löb<sup>3</sup>) and in alcoholic potassium-hydroxide solution at lead or mercury cathodes (Elbs<sup>4</sup>).

o-Nitroanisol, electrolyzed under the same conditions as

<sup>1</sup> Ber. d. deutsch. chem. Gesellsch. 28, 2349 (1895).

<sup>2</sup> Ibid. 27, 1931 (1894).

<sup>3</sup> Ztschr. f. Elektrochemie 2, 533 (1896).

<sup>4</sup> Journ. f. prakt. Chemie. 43, 39 (1891).

mentioned under *o*-nitrophenol, gives *o*-azoxyanisol, *o*-azoanisol, and *o*-hydrazoanisol (Häussermann,<sup>1</sup> Ells and Rohde<sup>2</sup>). It differs, therefore, from the above compound in this respect. *o*-Nitrophenol behaves similarly.

**m-Nitrophenol**, on being reduced, does not afford an opportunity for the quinone formation, and gives, hence, in alkaline solution *m*-azophenol. In alcoholic-sulphuric acid solution and at a lead cathode it is reduced to *m*-amidophenolsulphonic acid (Klappert<sup>3</sup>).

**p-Nitrophenol** behaves like the ortho-compound. According to Ells,<sup>4</sup> a good yield of *p*-amidophenol is produced in alkaline solution. Its ethers *p*-nitroanisol and *p*-nitrophenetol behave normally; they give chiefly the azoxy-derivatives, also some *p*-anisidine and phenetidine respectively.

Intermediate phases of the reduction can be separated in the case of *o*- and *p*-nitrophenol, if a concentrated solution of aniline hydrochloride is used as electrolyte (Job<sup>5</sup>). Complicated condensation products are obtained. It seems that the nitrosophenols primarily formed react in the form of quinone-oximes with aniline.

**p-Nitrophenol** thus gives as principal product diamidodiquinoneanil, a substance which is also produced in the reduction of *o*-nitrophenol, besides a blue induline-like dyestuff. The mechanism of this reaction has not yet been explained.

**o-p-Dinitrophenol**, on reduction in alcoholic-alkaline solution, gives a mixture of amidonitrophenol and diamidophenol (Ells<sup>6</sup>). A soluble red intermediate product is formed during the reaction.

**Trinitrophenol** (Picric acid) was reduced by Ells<sup>6</sup> in sulphuric-acid solution to picramic acid and diamidonitrophenol

<sup>1</sup> Chem. Ztg. 17, 209 (1893).

<sup>2</sup> Ztschr. f. Elektrochemie 7, 116 (1900).

<sup>3</sup> Ibid. 8, 791 (1902).

<sup>4</sup> Ibid. 7, 146 (1900).

<sup>5</sup> Ibid. 6, 441 (1900).

<sup>6</sup> Journ. f. prakt. Chem. [2] 43, 39 (1891).

## NITROPHENYL ETHERS.

Several representatives of this class of compounds were investigated as to their behavior in alkaline reduction (Häussermann and Schmidt<sup>1</sup>). These investigators confirmed the rules which Elb established for nitrophenyl ethers.

**o-Nitrophenyl ether, p-Nitrophenyl ether** are smoothly converted into azoxyphenyl ethers.

**p-Nitrophenyl-p-tolyl ether** gives similarly the p-azoxyphenyl p-tolyl ether.

**Hydroxyquinone-p-nitrodiphenyl ether** yields p-azoxydiphenyl ether.

p-Aminophenyl p-tolyl ether is smoothly formed from **p-nitrophenyl-p-tolyl ether** in hydrochloric-acid suspension with a tin cathode.

## V. Nitranilines.

**o-Nitraniline**, when electrolyzed in alkaline solution (Elbs and Rohde<sup>2</sup>) yields smoothly o-phenylenediamine, while the intermediately recurring nitroso- or hydroxylamine-phases, similar to those in the p-series, readily rearrange themselves into quinone derivatives.

**m-Nitraniline** behaves differently. This substance, by electrolysis in an alkaline electrolyte, gives a good yield of m-diaminoazobenzene (Elbs and Kopp,<sup>3</sup> and Löb<sup>4</sup>), also a little azoxy-compound and traces of m-phenylenediamine. The reduction can also be carried out to the hydrazo-phase. m-Nitraniline gives o-p-diamidophenol in sulphuric-acid solution (Gattermann).<sup>5</sup>

Rohde<sup>6</sup> has investigated the influence of methyl groups in the amido-groups in alkaline reduction.

**m-Nitradimethylaniline** gives tetramethyl-m-diamidoazobenzene, or the hydrazo-body. Voight<sup>7</sup> reduced it in con-

<sup>1</sup> Ber. d. deutsch. chem. Gesellsch. **34**, 3769 (1901).

<sup>2</sup> Ztschr. f. Elektrochemie **7**, 144, 340 (1900).

<sup>3</sup> Ibid. **5**, 110 (1898).

<sup>4</sup> Ibid. 439 (1899).

<sup>5</sup> Ber. d. deutsch. chem. Gesellsch. **26**, 1849 (1893).

<sup>6</sup> Ztschr. f. Elektrochemie **7**, 328, 338 (1900).

<sup>7</sup> Ztschr. f. angew. Chemie **107** (1894).

centrated sulphuric acid, and thus converted it into 1,3,4-dimethyl diamidophenol.

*m*-Nitrosodimethylaniline can be converted by Gattermann's process into *m*-p-dimethyldiamidophenol. Also *ch* 1.

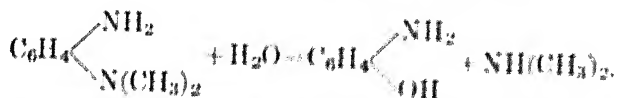
*m*-Nitromethylaniline behaves like *m*-nitrodiamethylaniline. It is converted in alkaline electrolytes into dimethyl *m*-diamidoazobenzene, or -hydrazobenzene.

**p-Nitraniline**, by reduction in concentrated sulphuric acid, cannot yield an amidophenol because the *p* position is occupied. Noyes and Dorrance<sup>2</sup> reduced it to *p*-diamidobenzene. *p*-Phenylenediamine is produced in alkaline solution, as might be expected (Ellbs).

The behavior of *p*-Aminoazobenzene may incidentally be mentioned here. This substance by electrolysis in acid solution with a tin cathode, or addition of stannous chloride, is smoothly converted into *p*-phenylenediamine,<sup>3</sup> in the same manner as *p*-nitraniline.

*p*-Nitroacetanilide. Sonnborn<sup>4</sup> observed the occurrence of diacetyl-*p*-diamidoazoxybenzene when this substance was reduced in alkaline solution. This agrees with the fact that the quinone formation from the reduction phases of *p*-nitroacetanilide is rendered difficult by the acetyl group. If on the contrary, the electrolyte is kept acid with acetic acid, the acetyl derivative of *p*-phenylenediamine and some phenylenediamine acetate are here also obtained.

*p*-Nitrodimethylaniline, in alcoholic-alkaline solution and at ordinary temperature, can be smoothly reduced to *p*-amido-dimethylaniline (Ronde<sup>5</sup>); at a higher temperature a splitting up into dimethylamine and *p*-amidophenol occurs.



<sup>1</sup> Ber. d. deutsch. chem. Gesellsch. 27, 1932 (1894)

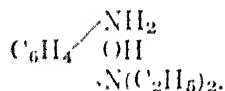
<sup>2</sup> Ibid. 28, 2349 (1895)

<sup>3</sup> D. R. P. No. 121835 (1900); See also 117607 (1900).

<sup>4</sup> Ztschr. f. Elektrochemie 6, 509 (1900).

<sup>5</sup> l. c.

*p*-Nitrodiethylaniline, by electrolytical reduction in concentrated sulphuric acid, is converted into the important intermediate product of dyestuff manufacture, *p*-amido-*m*-oxydiethylaniline.

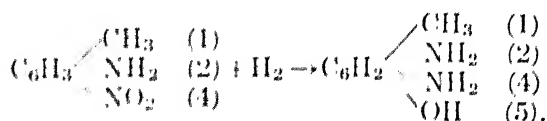


*p*-Nitrosodiethylaniline<sup>1</sup> gives the same compound.

#### NITROTOLUIDINES.

The nitrotoluidines when reduced electrolytically in acid and alkaline solution behave like the nitranilines. The position of the methyl group must, of course, be borne in mind.

*p*-Nitro-*o*-toluidine is converted by Gattermann's process<sup>2</sup> into diamidocresol:



In this case the hydroxyl group occupies the *o*-position in respect to the original nitro-group.

In alkaline reduction *p*-tolylenediamine is produced (Elbs).<sup>3</sup>

*o*-Nitro-*p*-toluidine in sulphuric acid solution gives the same diamidocresol as *p*-nitro-*o*-toluidine, the hydroxyl group occupying the para-position to the original nitro-group.

The electrical reduction in an alkaline electrolyte leads to a good yield of *o*-tolylenediamine. If the reduction is carried out in alkaline solution, *m*-nitro-*p*-toluidine and *m*-nitro-*o*-toluidine, as might be supposed, are converted into azoxy-, azo- and hydrazo-compounds.

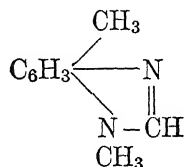
*m*-Nitrodimethyl-*p*-toluidine gives dimethylbenzimidazole (Pinnow<sup>4</sup>)

<sup>1</sup> D. R. P. No. 81625 (1894).

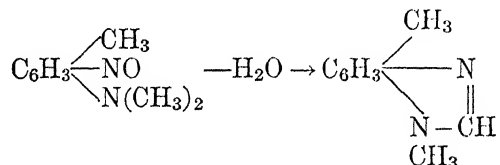
<sup>2</sup> Ber. d. deutsch. chem. Gesellsch. **26**, 1850 (1893).

<sup>3</sup> Ztschr. f. Elektrochemie **7**, 145 (1900).

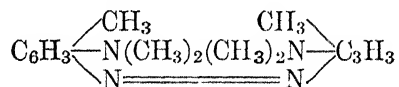
<sup>4</sup> Journ. f. prakt. Chemie **63**, 352 (1901); **65**, 579 (1902).



and dimethyltoluylenediamine. The reaction is carried out in Löb's short-circuit cell (p. 50). An addition of graphite powder accelerates the reaction, which probably is mainly caused by the intermediately occurring nitroso-compound splitting off water, and thus yielding the dimethylbenzimidazole,



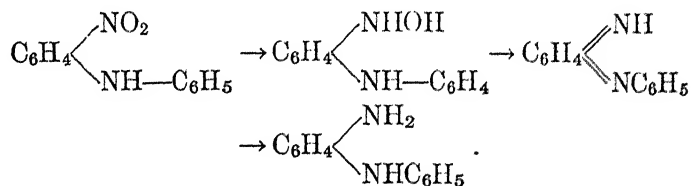
**m-Nitrodimethyl-o-toluidine.**—This substance, reduced in alkaline electrolytes, gives tetramethyl-m-diamido-p-azotoluene.



and tetramethyl-m-diamido-p-hydrazotoluene.

#### VI. Nitro-derivatives of Diphenylamine and Amidotriphenylmethane.

**p-Nitrodiphenylamine**, by reduction in alcoholic-alkaline solution according to Elbs' method, gives a good yield of p-amido-diphenylamine (Rohde<sup>1</sup>); the primary production of quinone probably prevents the formation of the azoxy-compound:



**Benzoyl-p-nitrodiphenylamine** cannot yield a quinonedi-

<sup>1</sup> Ztschr. f. Elektrochemie 7, 329 (1900).

imido-derivative. Benzoyl-*p*-azoxydiphenylamine as well as the azo-compound are hence produced if a saponification of the benzoyl group by the free alkali is prevented by neutralizing with acetic acid, or if ammonium acetate is employed in place of the sodium acetate in the cathode fluid.

***p*-Nitrodiamidotriphenylmethane**, on electrolytic reduction in concentrated sulphuric acid by a method of the Gesellschaft für Chem. Industrie in Basel<sup>1</sup> can be converted into *p*-rosaniline. The method is of general applicability: carbinols  $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{C}(\text{OH})\text{R}_2$  result in the reduction of nitro-leucobodies of the type  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{C}(\text{H})\text{R}_2$ . (In these formulæ R denotes aromatic radicals with primary, secondary, or tertiary amido-groups, or with hydroxyl-groups.)

Thus is formed *p*-nitro-bitter-almond-oil-green from *p*-nitro-tetramethyldiamidotriphenylmethane.

Besides the mentioned products serving as the starting-point, there were also used *p*-nitrodiamido-*o*-ditolyl-methane, *p*-nitrotetramethyldiamidotriphenyl-methane, and other analogous compounds.

#### VII. Nitroaldehydes and Nitroketones.

**Nitrobenzaldehyde.** Kaufmann and Hof<sup>2</sup> subjected *m*-nitrobenzaldehyde to reduction in alkaline-alcoholic solution and thus obtained *m*-azobenzoic acid as the principal product and *m*-azobenzyl alcohol as a secondary product. Since the yield of the latter is extremely small when compared with that of the former, the authors assumed that there occurred a further destructive action of the alkali on the primarily formed nitrobenzyl alcohol in such a way that 8 molecules of the alcohol give 1 molecule azoxybenzyl alcohol and 3 molecules azoxybenzoic acid. These substances are then converted by the further action of the current into the corresponding azo-compound, thus increasing considerably the quantity ratio of the primarily formed acid in comparison with the alcohol (see p. 188). By pursuing this reaction further Löb<sup>3</sup> was led to a synthesis of mixed azo-compounds; these will be mentioned later. If

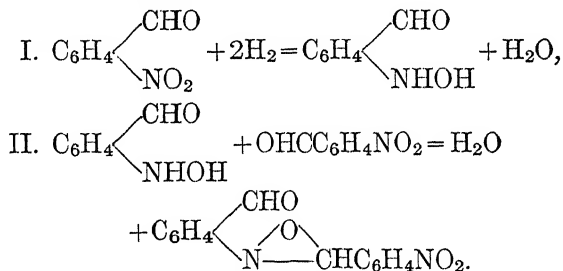
<sup>1</sup> D. R. P. No. 84607 (1894).

<sup>2</sup> Chem. Ztg. 20, 242 (1896).

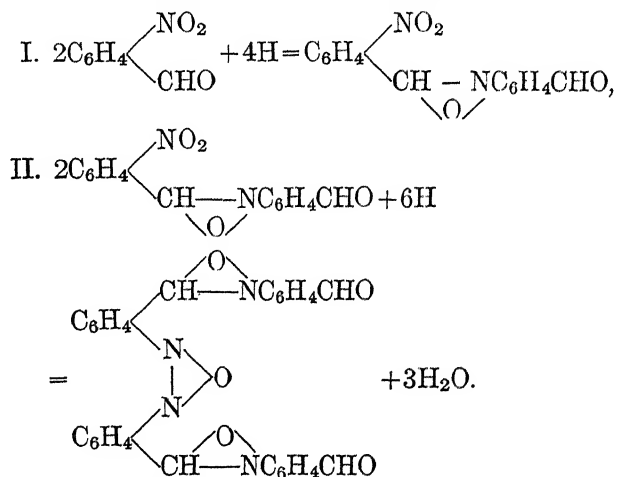
<sup>3</sup> Ztschr. f. Elektrochemie 5, 456 (1899).



nitroaldehydes are reduced in sulphuric-acid solution, either the free aldehydophenylhydroxylamines, or their condensation products with unchanged nitroaldehyde, i.e., nitrobenzylidenealdehyde-phenylhydroxylamines, are formed. *m*- and *p*-Nitrobenzaldehyde were investigated. The formation of these bodies is expressed by the following equations:



On further reduction the process can again repeat itself, so that similar higher molecular compounds are formed. The nitrobenzylidenealdehydophenylhydroxylamines are produced from the two mentioned aldehydes. If the *p*-nitrobenzaldehyde is reduced beyond the compound mentioned in the equation, the *n*-*p*-formylphenyl ether of *p*-azoxybenzaldoxime is formed (Always <sup>1</sup>), as shown in the following equations:



<sup>1</sup> Ber. d. deutsch. chem. Gesellsch. 29, 3037 (1896); 36, 23 (1903); Ztschr. f. Elektrochemie 3, 373 (1897).

In the reduction of aromatic nitroketones in concentrated sulphuric acid the normal reaction, i.e., the formation of p-amidophenol derivatives, occurs (Gattermann <sup>1</sup>).

**m-Nitroacetophenone** gives amidooxyacetophenone.

**m-Nitrobenzophenone** and **m-nitrophenyl-p-tolylketone** give analogous bodies.

In alkaline-alcoholic solution Elbs and Wogrinz <sup>2</sup> obtained m-azoxy- and m-azoacetophenone from m-nitroacetophenone. The reduction to the hydrazophase was only partially successful.

By using a copper cathode with addition of copper sulphate, in place of the previously employed nickel gauze cathode, a good yield of m-aminoacetophenone is obtained in sulphuric acid solution; in alkaline solution a poor yield results.

**m-Nitrobenzophenone**, on electrolysis in alkaline solution at ordinary temperature, gives an almost quantitative yield of m-azoxybenzophenone; when reduced at the boiling temperature, a good yield of m-azobenzophenone is obtained, while in sulphuric-acid solution m-aminobenzophenone readily results. In the above processes the carbonyl group apparently does not participate in the reduction of the nitroketones.

#### VIII. Nitrobenzenecarboxylic Acids.

**Nitrobenzoic Acids.**—The m- and p-acids, by reduction in alkaline solution, are smoothly and almost quantitatively converted into the corresponding azo-acids, while the o-acid, according to Löb's <sup>3</sup> researches, under similar conditions yields o-azoxy- and o-hydrazobenzoic acid and complex blue decomposition products. This deportment is of particular interest because the o-acid also occupies an exclusive position in the *chemical* reduction, and similar experiences seem to repeat themselves with the nitrobenzenesulphonic acids (Gattermann <sup>4</sup>).

In dilute sulphuric acid Hostmann <sup>5</sup> converted o-nitro-

<sup>1</sup> Ber. d. deutsch. chem. Gesellsch. **29**, 3034 (1896).

<sup>2</sup> Ztschr. f. Elektrochemie **9**, 428 (1903).

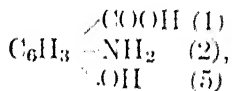
<sup>3</sup> Ibid. **2**, 532 (1896).

<sup>4</sup> Ibid. **10**, 581 (1904).

<sup>5</sup> Chem. Ztg. **17**, 1099 (1893).

benzoic acid into *o*-azo-, hydrazobenzoic acid and anthranilic acid.

In concentrated sulphuric acid oxyanthranilic acid,



is produced by the method of Gattermann,<sup>1</sup> from the ortho acid; 1·3·6-amidosalicylic acid is formed from the meta-acid.

*p*-Nitrobenzoic acid, according to Clement and Noye<sup>2</sup> gives the *p*-amidophenolsulphonic acid when electrolyzed in very concentrated sulphuric acid.

The *o*- and *m*-nitrobenzoic esters, on electrolysis, behave themselves like the free acids (Gattermann). The latter investigator,<sup>3</sup> by preparing the benzylidene compound by the usual method, proved the intermediate formation of the hydroxylamine phase in the reduction of the *m*-acid.

The experiments of Schall and Klein<sup>4</sup> concerning the formation of nitrobenzene from *o*-nitrobenzoic acid are quite interesting. If a solution of soda in molten *o*-nitrobenzoic acid (carbon acid escapes during the solution process, so that a solution of the sodium salt in the acid itself is obtained) is electrolyzed at 200° and at platinum electrodes, relatively large quantities of nitrobenzene are produced; at the same time a gas is evolved at the anode (CO<sub>2</sub>?). During an electrolysis lasting one or two hours, with 0.8 to 1 amp., about 1 cc. was obtained. These experiments were made with the expectation of finding a reaction among the aromatic acids similar to Kolbe's. Although in the case of the aliphatic acids a limit hydrocarbon is formed by the union of two anions with splitting off of carbonic acid, for instance,



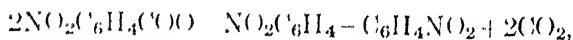
<sup>1</sup> Ber. d. deutsch. chem. Gesellsch. **26**, 1850 (1893); **27**, 1932 (1894).

<sup>2</sup> Am. Chem. Journ. **16**, 511 (1894).

<sup>3</sup> Ber. d. deutsch. chem. Gesellsch. **29**, 3040 (1896).

<sup>4</sup> Ztschr. f. Elektrochemie **5**, 256 (1898).

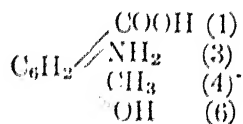
an analogously formed product, *o*-dinitrodiphenyl,



could not be obtained from *o*-nitrobenzoic acid.

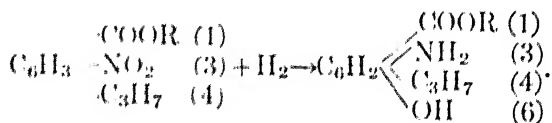
The following nitrobenzene carboxylic acids (or their esters) on reduction in concentrated sulphuric acid, react in a normal manner:

***m*-Nitro-*p*-toluic Acid.**<sup>1</sup> Amidoceresotinic acid is formed:



The methyl and ethyl esters behave analogously.

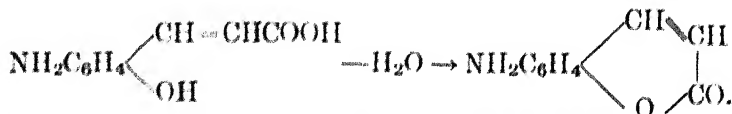
**Nitrocumic Methyl and Ethyl Esters** give the corresponding amidophenol esters:



#### NITROCINNAMIC ACIDS.

**Orthonitrocinnamic Acid.**—This substance, by reduction in concentrated sulphuric acid, is converted into the sulphate of amidoxyceinnamic acid which, on being heated in hydrochloric acid, is in turn converted into oxycarbostyryl. The methyl ester,<sup>1</sup> under like conditions, behaves similarly.

***m*-Nitrocinnamic Acid.** This acid, treated analogously, gives amidocoumarin, which is produced from the *m*-amidoxyceinnamic acid by a splitting off of water:



<sup>1</sup> Ber. d. deutsch. chem. Gesellsch. 26, 1851 (1893); 27, 1935 (1894).

The ethyl ester leads to the same compound—either by saponification of the nitro-ester before the reduction, or by the splitting off of alcohol from the intermediately formed amidooxycinnamic ester.

#### NITROPHTHALIC ACIDS

**$\alpha$ -Nitrophthalic Acid** was converted by Ellbs'<sup>1</sup> method into azo- and hydrazophthalic acid; traces of  $\alpha$ -aminophthalic acid were also produced.

**$\beta$ -Nitrophthalic Acid** behaves similarly.

**Nitroisophthalic Acid.** This substance, by electrolytic reduction in concentrated sulphuric acid, according to Gattermann,<sup>2</sup> is converted into the sulphate of oxyamidoisophthalic acid. *Nitroterephthalic acid* gives an amidooxyterephthalic acid.

#### NITROBENZONITRILES

**m-Nitrobenzonitrile** can be converted by Ellbs'<sup>3</sup> method, depending upon the conditions of the experiment, either without saponification into m-azobenzonitrile, or with saponification into m-azoxybenzamide and m-azobenzamide.

**p-Nitrobenzonitrile** gives analogously azo- and azoxybenzamide or azo- and azoxybenzamide.

#### IX. Nitrobenzenesulphonic Acids.

Those sulphonic acids which have the  $\text{SO}_3\text{H}$ -group in the m-position to the nitro-group, have been particularly investigated. Under the conditions chosen by Ellbs,<sup>4</sup> they yield universally azo- and hydrazo-bodies. Thus *nitrobenzene-m-sulphonic acid*, *o-nitrotoluene-p-sulphonic acid*, *p-nitrotoluene-m-sulphonic acid* are converted into the corresponding azo- or hydrazo-compounds.

**p-Nitrobenzenesulphonic Acid** also behaves normally on electrolytic reduction in slightly alkaline solution at nickel cathodes (Ellbs and Wohlfahrt<sup>5</sup>); it yields azo-, or hydrazo-

<sup>1</sup> Ztschr. f. Elektrochemie 7, 143 (1900).

<sup>2</sup> Ber. d. deutsch. chem. Gesellsch. 26, 1852 (1893).

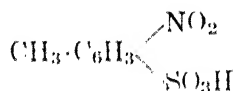
<sup>3</sup> Ztschr. f. Elektrochemie 7, 143 (1900).

<sup>4</sup> Ibid. 7, 142 (1900).

<sup>5</sup> Ibid. 8, 789 (1902).

acid. In the case of the *o*-nitro-acid, on the contrary, the reduction is far from normal; complicated products and *o*-aminosulphonic acid are chiefly produced.

**p-Nitrotoluenesulphonic Acid.** The Gesellschaft f. Chem. Industrie of Basel<sup>1</sup> prepares orange dyes by using as cathode fluid an alkaline solution of the yellow condensation products of *p*-nitrotoluenesulphonic acid,



(e.g. a mixture of azoxystilbenedisulphonic acid, azostilbenedisulphonic acid, and dinitrostilbenedisulphonic acid). The reduction, however, must not be continued until amido-compounds result.

Ellis and Kreman<sup>2</sup> have likewise investigated the electrochemical behavior of the dye "sun yellow" formed in alkaline solution of the *p*-nitrotoluenesulphonic acid, and found the following:

1. "Sun yellow" consists chiefly of *p*-azoxystilbenedisulphonic acid.
2. Reduced in alkaline solution it yields as end product, *p*-azotoluenedisulphonic acid.
3. In acid solution with addition of stannous chloride there are formed *p*-diaminostilbenedisulphonic acid and *p*-toluidinesulphonic acid.

The following may be remarked concerning the reduction in acid solution: According to Häussermann,<sup>3</sup> metanilic acid is smoothly obtained from *m*-nitrobenzenesulphonic acid in dilute sulphuric acid; in concentrated acid 3,4-amidophenolsulphonic acid results (Gattermann<sup>4</sup>).

***o*-Nitrotoluene-*p*-sulphonic Acid** gives similarly 2·4·5-amino-cresolsulphonic acid.

<sup>1</sup> Eng. Pat. No. 22482 (1895).

<sup>2</sup> Ztschr. f. Elektrochemie **9**, 416 (1903).

<sup>3</sup> Chem. Ztg. **17**, 209 (1893).

<sup>4</sup> Ber. d. deutsch. chem. Gesellsch. **27**, 1938 (1894).

**p-Dinitrostilbenedisulphonic Acid** (according to Elber-Kremann<sup>1</sup>), like *p*-azostilbenesulphonic acid, yields in alkaline solution *p*-azotoluenedisulphonic acid, while in acid solution with the addition of stannous chloride the end-product is diaminodibenzylsulphonic acid.

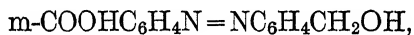
**p-Dinitrodibenzylsulphonic Acid** yields in alkaline solution *p*-azodibenzylsulphonic acid; in acid solution, in the presence of stannous chloride, *p*-diaminodibenzylsulphonic acid.

#### X. Other Reductions of Nitro-compounds.

Löb<sup>2</sup> has utilized the possibility of conducting the reduction in alkaline solution up to the azo-phase for accomplishing the direct electrosynthesis of mixed azo-bodies and azo-dyes.

The components of the desired compounds are reduced in equimolecular proportions under conditions which make possible the union of the two radicals during the azo-phase. By means of this method azo-compounds in which the substituents are in any desirable position to the azo-bond, and which are not obtainable by the Griess method, can be prepared.

Thus *m*-nitrobenzaldehyde, which in alkaline solution gives equal molecules of *m*-nitrobenzoic acid and *m*-nitrobenzyl alcohol, yields as chief product *m*-*m*-azobenzoic-acid-benzyl alcohol,



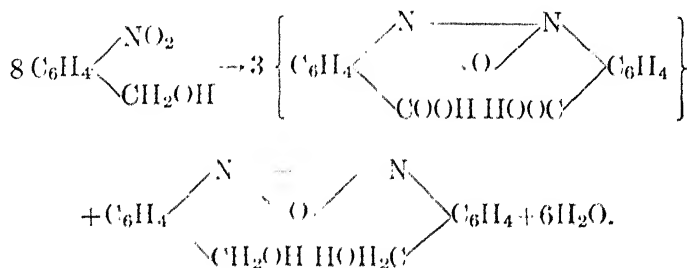
and as secondary products *m*-azobenzoic acid and *m*-azobenzyl alcohol.

Kaufmann and Hof<sup>3</sup> (p. 181) had subjected *m*-nitrobenzaldehyde to reduction in alkaline solution, but they did not observe the occurrence of the mixed azo-compound; they obtained only the azo-alcohol and the azo-acid, and explained the low yield of the former by the behavior of the *m*-nitrobenzyl radical towards alkalis, as shown in the equation:

<sup>1</sup> l. c.

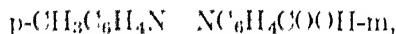
<sup>2</sup> Ber. d. deutsch. chem. Gesellsch. **31**, 2201 (1898); Ztschr. f. Elektrochem. **15**, 456 (1899).

<sup>3</sup> Chem. Ztg. **20**, 242 (1896).



Of the other bodies prepared by Löb according to the principle mentioned, the following may be noted:

Azo-*p*-toluene-*m*-benzoic acid,



is prepared from *p*-nitrotoluene and *m*-nitrobenzoic acid.

*m*-*m*-Sulphoazobenzoic acid,

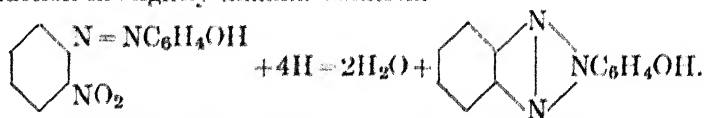


is obtained from *nitrobenzenesulphonic acid* and *nitrobenzoic acid* in a pure state and in the form of the acid potassium salt. The latter, which can be crystallized from alcohol, can be obtained by neutralizing the electrolyte with hydrochloric acid and concentrating the solution.<sup>1</sup>

*o*-Methylazobenzene is formed from *o*-nitrotoluene and *nitrobenzene* as a red oil boiling at 185°-188° at 28 m.m. pressure.

The mixed azo-compounds are always formed in company with the azo-derivatives of the components, so that their yields are often not very favorable.

Elbs and Keiper<sup>2</sup> have found that *o*-nitroazo-compounds are smoothly converted into phentriazoles by electrochemical reduction in slightly alkaline solution.



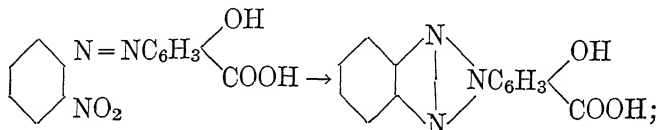
<sup>1</sup> Recent experiments by van Emster, Bonn (1904).

<sup>2</sup> Journ. f. prakt. Chemie 67, 580 (1903).



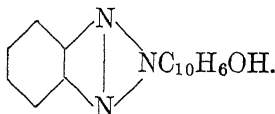
There result from

**o-Nitrobenzeneazophenol**, phenolphentriazole; from  
**o-Nitrobenzeneazosalicylic acid**, salicylic-acid-phentriazole,



and from

**o-Nitrobenzeneazo- $\alpha$ -naphthol**,  $\alpha$ -naphtholphentriazole:



## XI. Nitro-Derivatives of the Naphthalene, Anthracene, and Phenanthrene Series.

Since only the nitro-group is subject to reduction by the cathodic action of the current on nitro-compounds, nothing new can here be added regarding the possible reduction phases. The conditions which with the benzene derivatives lead to certain stages, cannot always be directly applied to these substances; this is due to the influence which the whole molecule possesses over the reaction velocity of the separate processes. This deportment is especially shown by the nitro-derivatives of the anthracene series. Nevertheless, some of the more general conditions also obtain here; for instance, nitronaphthalene derivatives in acid electrolytes at attackable cathodes, according to the process of Boehringer & Söhne,<sup>1</sup> are also easily reduced to amines. Gattermann's method has also been serviceable in the preparation of amidonaphthols.

**$\alpha$ -Nitronaphthalene,**<sup>2</sup> in aqueous acetone solution was reduced by Voigt to nitrosostyrol besides a little naphthylamine. The latter is quantitatively obtained if  $\alpha$ -nitronaphthalene is

<sup>1</sup> D. R. P. No. 116942 (1899); 117007 (1900)

<sup>2</sup> Ztschr. f. angew. Chemie (1894) 108.

reduced in a hydrochloric-acid electrolyte with an attackable cathode, or with addition of salts of the latter.<sup>1</sup>

$\alpha_1$ -Nitronaphthalene- $\alpha_3$ -sulphonic acid was converted by Voigt<sup>2</sup> into hydrazonaphthalenesulphonic acid and some naphthylamine. Gattermann<sup>3</sup> obtained by his method the aminonaphtholsulphonic acid in a normal manner. Analogously behave

$\alpha_1$ -Nitronaphthalene- $\beta_3$ - and  $\beta_4$ -sulphonic acids and the disulphonic acids ( $\beta_2$ ,  $\beta_3$ , and  $\beta_2\beta_4$ ) of  $\alpha$ -Nitronaphthalene.<sup>4</sup>

( $\alpha_1\alpha_4$ )Dinitronaphthalene (according to a patent of the Badische Anilin- u. Sodafabrik) alone, or mixed with ( $\alpha_1\alpha_2$ )dinitronaphthalene, gives in concentrated sulphuric-acid solution a product which, by heating with dilute acids, can readily be converted into naphthazarin.<sup>5</sup>

$\alpha_1\alpha_3$ - and  $\alpha_1\alpha_4$ -Dinitronaphthalene, if reduced according to Tafel, in a mixture of acetic and sulphuric acid with prepared lead cathodes, gives the 1-5- and 1-8-naphthylenediamines (Möller<sup>6</sup>).

$\alpha$ -Nitro- $\beta$ -naphthyl ethyl ether,  $C_{10}H_6 \begin{matrix} \nearrow NO_2 \\ \searrow OC_2H_5 \end{matrix}$ .—This naph-

thol ether, unlike the nitrophenol ethers, gives  $\alpha$ -amido- $\beta$ -naphthyl ethyl ether as end-product of the alkaline reduction (Rhode<sup>7</sup>).

o-Nitroanthraquinone has been reduced by Möller<sup>8</sup> in alcoholic-sulphuric acid and in slightly alkaline solution to o-amidoanthraquinone. By electrical oxidation in concentrated sulphuric acid there is formed, according to Weizmann,<sup>9</sup> nitro-oxyanthraquinone; with alternating currents alizarinamide was produced; and in the presence of glycerin, mannit, etc., blue and

<sup>1</sup> D. R. P. No. 116942 (1899); 117007 (1900)

<sup>2</sup> Ztschr. f. angew. Chemie. 1894, 108.

<sup>3</sup> Ber. d. deutsch. chem. Gesellsch. 26, 1852 (1893).

<sup>4</sup> D. R. P. No. 81621 (1893).

<sup>5</sup> D. R. P. No. 79406 (1894).

<sup>6</sup> Elektrochem. Ztschr. 10, 199, 222 (1903-1904).

<sup>7</sup> Ztschr. f. Elektrochemie 7, 340 (1900).

<sup>8</sup> Ibid., 741, 797 (1901).

<sup>9</sup> Fr. P. No. 265292 (1897).

green reduction products resulted. The action of the cathodic current on

**1·2-Dinitroanthraquinone** and **1·5-Dinitroanthraquinone** in a solution of glacial acetic acid with addition of sulphuric acid produces diamidoanthraquinones;<sup>1</sup> the yield, however, is poor. The employment of lead cathodes, as shown by Tafel, may perhaps increase the latter.

According to experiments of the Badische Anilin- u. Soda-fabrik,<sup>2</sup> a dinitroanthraquinone dissolved in fuming sulphuric acid is changed by electrolytic reduction to blue mordant dyes.

**Dinitroanthrarufindisulphonic Acid** and **Dinitrochrysazindisulphonic Acid**.—These substances are easily reduced electrolytically in sulphuric-acid solution to diamidoanthrarufindisulphonic acid and diamidochrysazindisulphonic acid.<sup>3</sup>

**9-Nitrophenanthrene** has been converted by Schmidt and Strobel<sup>4</sup> into 9-azoxyphenanthrene by Elbs' process.

**2-Nitrophenanthrenequinone** in acid solution at lead cathodes gives 2-aminophenanthrenequinone (Möller).

**2·7-Dinitrophenanthrenequinone** is converted in acid solution into 2·7-diamidophenanthrenequinone (Möller).

## XII. Nitroso- and Nitro-Derivatives of the Pyridine and Quinoline Series.

**Nitrosopiperidine**, on electrolytic reduction in sulphuric-acid solution (Ahrens<sup>5</sup>), gives piperylhydrazine, piperidine, and ammonia; at the anode there are formed at the same time a diamine,  $C_{10}H_{18}N_2$ , of the fatty acid series, and two isomeric amidovaleric acids, besides hydrochloric acid and piperidine. Under similar conditions

**Nitroso- $\alpha$ -pipecoline** gives  $\alpha$ -methylpiperylhydrazine,  $\alpha$ -pipecoline and ammonia at the cathode, and at the anode a

<sup>1</sup> Elektrochem. Ztschr. **10**, 199, 222 (1903-1904).

<sup>2</sup> D. R. P. No. 92800, 92998 (1896).

<sup>3</sup> D. R. P. No. 105501 (1898).

<sup>4</sup> Ber. d. deutsch. chem. Gesellsch. **36**, 2512 (1903).

<sup>5</sup> Ztschr. f. Elektrochemie **2**, 578 (1896); Ber. d. deutsch. Gesellsch. **30**, 533 (1897); **31**, 2272 (1898).

diamine and an amidocaproic acid. In the same manner the other nitroso-derivatives of homologous piperidines on electrical reduction give corresponding piperylhydrazines.

Ahrens and Sollmann<sup>1</sup> similarly prepared from

**Nitroso- $\beta$ -pipecoline** the  $\beta$ -pipecolyldiazine; from

**Nitroso- $\gamma$ -pipecoline** the  $\gamma$ -pipecolyldiazine; from

**Nitroso- $\alpha$ - $\alpha$ -lupetidine** the  $\alpha$ - $\alpha$ -dimethylpiperylhydrazine; from

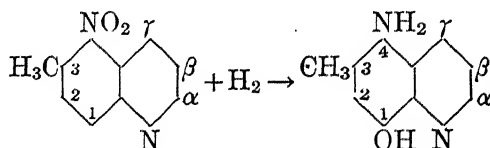
**Nitrosoaldehydecopellidine** the aldehydecopellidinediazine; and from

**Nitroso-s-trimethylpiperidine** the s-trimethylpiperylhydrazine.

**Nitrosotetrahydroquinoline.**—Concerning the experiments of Ahrens and Widera<sup>2</sup> on the oxidation of nitroso-derivatives of pyridine and quinoline there is yet to be mentioned the smooth conversion of nitrosotetrahydroquinoline into tetrahydroquinoline. The nitroso-group is found as nitric acid in the anode fluid.

**4-Nitroquinoline** and **1-o-Nitroquinoline**, reduced in concentrated sulphuric acid, give 1,4-oxyamidoquinoline and 1,4-amidooxyquinoline (Gattermann<sup>3</sup>).

**4-Nitro-3-toluquinoline** gives likewise a 4-amido-1-oxy-3-toluquinoline.



### 3. AMINO-DERIVATIVES.

**Aniline.**—Rotondi<sup>4</sup> electrolyzed aniline in an ammoniacal solution. After a period of three days, during which hydrogen was continually evolved at the negative pole and a tarry sub-

<sup>1</sup> Chem. Ztschr. **2**, 414 (1903).

<sup>2</sup> Ber. d. deutsch. chem. Gesellsch. **31**, 2276 (1898).

<sup>3</sup> Ibid. **27**, 1939 (1894).

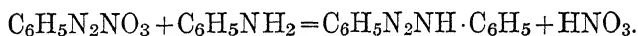
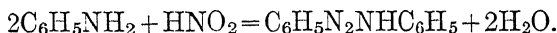
<sup>4</sup> Jahresh. f. Chemie, 1884, 270.

stance was deposited at the positive pole, Rotondi interrupted the electrolysis and was able, with more or less certainty, to establish the following processes:

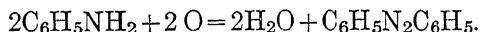
1. The formation of diazo-compounds:



2. The formation of diazoamido-compounds:



3. The formation of azo-compounds by direct oxidation of aniline:



4. The formation of amidoazo-compounds by molecular rearrangement of diazoamido-compounds. The nitrous acid and nitric acid were oxidation products of the ammonia which was added.

C. F. Boehringer & Söhne add a manganese salt to the electrolyte<sup>1</sup> in the presence of a strongly dissociating acid and thus smoothly oxidize aniline to quinone.

The fact that aromatic amines are often directly convertible by oxidation into dyes, early directed attention to the electrolytic oxidation of amines for the direct preparation of dyes. The investigations of Goppelsröder,<sup>2</sup> which were carried out some time ago, have primarily this end in view.

Goppelsröder has compiled the technical results in a small pamphlet: "Farbelektrochemische Mitteilungen" (Mühlhausen, 1889). They may be briefly mentioned here.

If a galvanic current is conducted through acid or neutral aqueous solutions of aniline, there is formed at the positive

<sup>1</sup> D. R. P. No. 117129 (1900).

<sup>2</sup> Dringler, Polytechn. Journ. **221**, 75; **223**, 317, 634; **234**, 92, 209 (1876)-1877). Cf. also: Concerning the Preparation of Dyes, and their Simultaneous Formation and Fixation in the Fibers with the Aid of Electrolysis, Goppelsröder, Reichenberg, 1885.

pole, besides other coloring matters, aniline black,  $C_{24}H_{21}N_4Cl$ . Under similar conditions dyes are obtained at the positive pole from the salts of *toluidine*, *methylaniline*, *diphenylamine*, *di-tolylamine*, and *phenyltolylamine*.

On electrolysis of a mixture of anthraquinone and caustic potash Goppelsröder obtained alizarine.

The numerous experiments which led to the formation of dyes at the anode, when aniline, toluidine, methylaniline, diphenylamine, *methyldiphenylamine* and *naphthylamine* or their salts were electrolyzed, have, however, not been scientifically investigated and, hence, still remain unsolved. The same holds true of Goppelsröder's investigations concerning the oxidation of phenol and anthraquinone. The most important discovery is the fact that aniline salts smoothly yield aniline black at the anode; the naphthylamine salts give naphthylamine-violet.<sup>1</sup>

Voigt,<sup>2</sup> by the electrolytic oxidation of suitable mixtures of bases, prepared rosaniline, chrysaniline, safranine, and p-leucaniline. His object in these researches was the same as that of Goppelsröder; namely, the preparation directly in the bath of the important dyes of the aniline series.

<sup>1</sup> The following literary data will serve as a guide:

*Research 1.\** Preparation of aniline black.

*Research 2.†* Electrolysis of aniline with excess of aniline.

Electrolysis of toluidine.

Electrolysis of mixtures of aniline with toluidine isomers.

*Research 3.‡* Electrolysis of aniline and toluidine salts in the presence of potassium nitrate, nitrite, or chlorate in aqueous solution.

*Research 4.§* Electrolysis of the salts of methylaniline.

Electrolysis of the salts of diphenylamine.

Electrolysis of the salts of methyldiphenylamine.

Electrolysis of phenol.

Electrolysis of the salts of naphthylamine.

*Research 5.||* Conversion of anthraquinone into alizarine by the electrolysis of a mixture of anthraquinone and potassium hydroxide.

<sup>2</sup> *Ztsch. f. angew. Chemie*, 1894, p. 107.

\* Dinger, *Polytechn. Journ.* **221**, 75 (1876).

† *Ibid.* **223**, 317 (1877).

‡ *Ibid.* **223**, 634 (1877).

§ *Ibid.* **224**, 92 (1877).

|| *Ibid.* **224**, 209 (1877).

If electrolytic oxygen is permitted to act upon aniline in concentrated acetic-acid solution, acetanilide is formed (Voigt); by using a dilute solution, however, amidohydroquinone is obtained.

These investigations have not been satisfactorily concluded, which is also the case with those of Foelsing,<sup>1</sup> who, by the oxidation of p-phenylenediamine and benzene-p-phenylenediamine, obtained indigo-blue dyes.

According to Löb's<sup>2</sup> experiments (see p. 176) by electrolytic reduction of nitro-compounds in a solution of fuming hydrochloric acid in an excess of an aromatic amine, induline-like dyes—not identical with the known induline dyes—are obtained. Szarvasy,<sup>3</sup> however, by anodic electrolysis of molten aniline hydrochloride, obtained electrolytically the indulines themselves. If a mixture of aniline and aniline hydrochloride is electrolyzed at 70°–90°, there is obtained a rich yield of azophenine, the known intermediate product of the indulines. By electrolysis of the pure molten salt at about 150°–300°, induline, anilidoinduline, and induline 6 B, besides the intermediate products of the induline formation, could be detected as products of the anodic oxidation. The oxidizing agent in these processes, which were carried out without an oxygen-containing electrolyte, was chlorine, which probably first produces azo-compounds that react further in the molten mass with aniline hydrochloride.

The interesting research of Votocek, Zenisek<sup>4</sup> and Sebor<sup>5</sup> may also be referred to in this connection. This permits the Sandmeyer-Gattermann reaction (substitution of the diazo-group by chlorine and bromine) to be carried out electrolytically. For this purpose the diazotized solution of the amine is electrolyzed—for instance 50 g. aniline, 120 g. HCl, 38.5 g. NaNO<sub>2</sub>—between copper electrodes with addition of cuprous chloride or copper sulphate. At the end of the experiment (ceasing of the nitrogen

<sup>1</sup> Ztschr. f. Elektrochemie 2, 30 (1895).

<sup>2</sup> Ibid. 6, 441 (1900).

<sup>3</sup> Ibid. 6, 403 (1900).

<sup>4</sup> Ibid. 5, 485 (1899).

<sup>5</sup> Ibid. 7, 877 (1901).

evolution) 64% chlorbenzene and 10% azobenzene could be isolated. This process could be used successfully for obtaining brombenzene by addition of copper sulphate and potassium bromide, also for p-chlortoluene and  $\beta$ -chlornaphthalene. The method is not applicable for preparing fluorbenzene and  $\alpha$ -chlornaphthalene.

The direct diazotization and preparation of *azo-dyes* in one electrochemical process was discovered by Löb.<sup>1</sup> His method—an anodic process—is based on the following principle:

As is well known, *azo-dyes* are generally prepared by diazotizing the amine in acid solution or suspension at a low temperature and then bringing together the diazotized solution with the usually alkaline solution of the components to be joined.

The same effect can be reached electrochemically, if amine, nitrite, and the coupling components of the compound desired are simultaneously exposed in a neutral or sometimes alkaline electrolyte to the anodic action of the current at an unattackable electrode.

The first stage of the process consists undoubtedly in the action of the discharged  $\text{NO}_2$  ions on the amine, as shown in the equation



However, if an amine alone is subjected to the anodic current action in the presence of the nitrite, complicated products result; besides the action of the  $\text{NO}_2$  ions upon the amido-group and the typical decomposition of the diazo-body by the electrolyte, substitution and oxidation processes seem to occur.

It is therefore necessary to add components to the electrolyte already before the electrolysis, which react so rapidly with the intermediately occurring diazo-bodies that the latter is withdrawn from the other disturbing influences.

Phenols are particularly suited as addition substances for fixing the diazo-bodies. Experiments have shown that the coupling of the diazo-compound with the acid component takes

<sup>1</sup> Ztschr. f. Elektrochemie 10, 237 (1904).



place much more rapidly than its decomposition by the mentioned influences. In the presence of phenols the formation of the azo-dyes can therefore be made the predominating one. It is very evident that in this process amines are not applicable as components for coupling purposes, because they are themselves subject to the action of the nitrite ions, and other complicated reactions.

The experiments are generally conducted by putting the aqueous solution, or suspension, of amine, coupling component—preferably in the form of a soluble salt—and nitrite, in equimolecular proportions, in the anode chamber, which is suitably separated from the cathode chamber by a diaphragm. Platinum is the best anode material; any suitable metal can serve as cathode. The current conditions chosen may vary greatly—from 50–600 amp. per square meter of anode surface. It is very important that the anode fluid be stirred during the whole experiment.

An increase in temperature is sometimes beneficial, but is generally unfavorable for the yield and purity of the dyes. An artificial lowering of the temperature, which is necessary for the chemical diazotizing process, is never required. Several examples are classified in the following table:

Anode solutions:	Sodium Sulphanilate $\beta$ -Naphthol Sodium Nitrite Water	Benzidine Naphthionate Sodium Nitrite Water Sodium Hydroxide	Dianisidine $\beta$ -Naphthol Sodium Nitrite Water	Benzidine Sodium Salicylate Sodium Nitrite Water	Sodium 1,4-Naphthylaminesulphonate. $\beta$ -Naphthol Sodium Nitrite Water
Results:	Orange II	Congo	Dianisidine-blue	Chrysamine G	Rocceline

**Dimethylaniline**, electrolyzed in sulphuric-acid solution at platinum electrodes in the presence of some chromic acid, gives tetramethylbenzidine. In this case the oxidizer is chromic

acid; the current action consists only in the continual regeneration of the latter (Löb<sup>1</sup>).

**Triamidotriphenylmethane.**—The Farbwerken vorm. Meister, Lucius, & Brüning,<sup>2</sup> by electrolytically oxidizing those substances which are formed in the treatment of the hydrochloric-acid salts of homologues of triamidotriphenylmethane with fuming sulphuric acid in the presence or absence of sulphur, succeeded in preparing blue, basic triphenylmethane dyes.

#### 4. PHENOLS.

**Phenol.**—Bunge,<sup>3</sup> Bartoli and Papasoli<sup>4</sup> submitted phenol to the action of the electric current. Bunge observed that the decomposition of potassium phenolate was analogous to that of an acid or a salt; the potassium phenolate was split up into K (cation) and  $C_6H_5O$  (anion), the latter combining with water to form phenol, with the liberation of oxygen. Bartoli and Papasogli, on electrolyzing solutions of phenol in potassium and sodium hydroxide, and using electrodes of coke, graphite, and platinum, obtained an acid having the composition  $C_7H_6O_4$ , which melted at  $93^\circ$ , reduced ammoniacal silver solution and Fehling's solution on being heated, and when in aqueous solution was not precipitated by acids. When, however, retort coke was used as the positive electrode, an extensive decomposition of the phenol occurred and a resin was formed.

On subjecting a neutral potassium phenolate solution to the action of the electric current they were able to isolate a compound,  $C_{65}H_{48}O_{22}$ , soluble in alkali and precipitated from such solutions by mineral acids. This latter compound on being oxidized with nitric acid formed picric acid. When allowed to remain in solution in the presence of dilute acids for a pro-

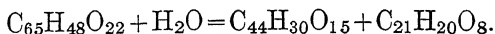
<sup>1</sup> Ztschr. f. Elektrochemie 7, 603 (1901).

<sup>2</sup> D. R. P. No. 100556 (1897).

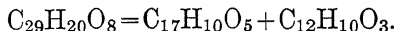
<sup>3</sup> Ber. d. deutsch. chem. Gesellsch. 3, 296 (1870).

<sup>4</sup> Gazz. chim. 14, 103 (1884).

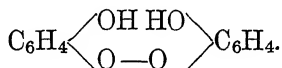
longed period, it underwent decomposition according to the following equation:



- The electrolysis of neutral sodium-phenolate solution gave an acid having the formula  $\text{C}_{29}\text{H}_{20}\text{O}_8$ , which likewise is decomposed on boiling with dilute acids:



The compound  $\text{C}_{12}\text{H}_{10}\text{O}_3$  is soluble in alcohol, melts at  $75^\circ$ , and is isomeric with the hydroquinone ether obtained by Étard from chlorchromic acid and phenol. It has the composition



The relations which exist between the potential and the pressure with which a discharged ion, like chlorine, bromine, or iodine reacts with phenol have been determined by Zehrlant<sup>1</sup> with the following results:

The substitution of chlorine in phenol in dilute acid solution does not take place, nor does that of bromine, since the oxidation begins earlier, at a lower potential, than the halogen discharge. Iodine also does not act on phenol in acid solution. A bromination can, however, be obtained if, on the one hand, the potential for the beginning of the oxidation is raised by decreasing the oxygen- or hydroxyl-ionic concentration; on the other hand, the discharge potential of bromine is lowered by increasing the bromine concentration, i.e., if concentrated hydrobromic acid (multiple normal) is employed, bromination occurs.

**Thymol.**—In alkaline solution halogen substitution takes place very rapidly with phenols. This fact has led to the

<sup>1</sup> Ztschr. f. Elektrochemie 7, 501 (1901).

electrolytic preparation of dithymoldiiodide, the antiseptic *aristol*, as made by Messinger and Vortmann<sup>1</sup> by the electrolysis of an alkaline solution of thymol with the addition of potassium iodide.

Directions for the preparation of a whole series of iodides of phenols are mentioned in the same patent papers; e.g., from *β-naphthol*, *phenol*, *resorcin*, *salicylic acid*, *cresotinic acid*, *carvacrol*, *p-isobutylphenol*, *o-m-p-isobutylcresol*, etc.

Nosophen, a tetraiodophenolphthaleïn, from phenolphthaleïn (Classen and Löb<sup>2</sup>), is obtained in like manner.

With these methods of preparation there corresponds a similar process, which the Société chimique des usines du Rhône and Gilliard, Monnet et Cartier patented in Germany,<sup>3</sup> for the electrolytic preparation of eosine and other halogen derivatives of the fluoresceïn group. The solutions of the fluoresceïns in alkali-hydroxide or in alkali-carbonate solution serve as anode fluids. The halogens, such as chlorine or bromine, are introduced into the anode compartment, whereby salts of the halogen acids form and simultaneous halogenation of the fluoresceïns occurs.

Since the salts are again decomposed by the current, with splitting off of the halogen, which in turn reacts on the fluoresceïns, the quantitative—very important for bromine and iodine—utilization of the halogen can take place. The well-known eosins are said to be obtained in excellent yields and in a high state of purity.

*Phenylmercaptan*.—Bunge,<sup>4</sup> who had obtained ethyldisulphide from ethyl mercaptan (see p. 65), also investigated phenylmercaptan. Phenyldisulphide,  $(C_6H_5)_2S_2$ , was formed from phenylmercaptan at the positive pole.

*Hydroquinone*.—If an acid hydroquinone solution with addition of a manganese salt, according to the process of C. F. Boehringer & Söhne,<sup>5</sup> is electrolyzed, quinone is smoothly pro-

<sup>1</sup> D. R. P. No. 64405 (1891).

<sup>2</sup> Ber. d. deutsch. chem. Gesellsch. **28**, 1603 (1895).

<sup>3</sup> D. R. P. No. 108838 (1899).

<sup>4</sup> Ber. d. deutsch. chem. Gesellsch. **3**, 911 (1870).

<sup>5</sup> D. R. P. No. 117129 (1900).

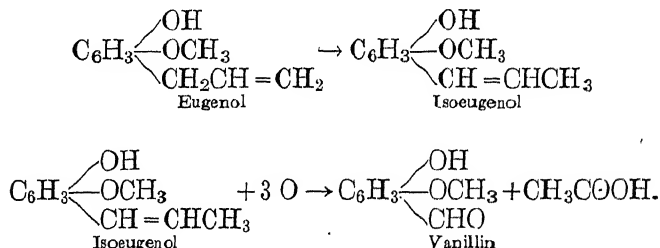
duced. But if a weak sulphuric-acid solution without addition is electrolyzed, quinonehydron is precipitated at the anode (Liebmann<sup>1</sup>).

**Resorcin.**—Alefeld and Vaubel,<sup>2</sup> by electrolytic oxidation, have obtained dyes of different shades from resorcin and other hydroxyl derivatives of the aromatic series, such as gallic acid, tannic acid, fluoresceins and eosins. An investigation of the dyes was not made.

**Pyrogallol (pyrogallie acid).**—According to A. G. Perkin and F. M. Perkin,<sup>3</sup> purpurogallin  $C_{11}H_8O_5$ , can readily be obtained by electrochemical oxidation of pyrogallol in dilute sulphuric acid with addition of sodium sulphate at a platinum-iridium anode.

**Gallic Acid** behaves likewise. Purpurogallincarboxylic acid,  $C_{11}H_7O_5COOH$ , is probably obtained.

**Eugenol.**—The firm v. Heyden Nchfg.<sup>4</sup> obtains vanillin electrolytically from eugenol. The latter is rearranged by alkalies into isoeugenol and then oxidized electrolytically in alkaline solution:



## 5. ALCOHOLS, ALDEHYDES, KETONES, AND QUINONES.

These classes of bodies, owing to their peculiarity in being both reducible and oxidizable, present many interesting phenomena respecting their electrolytic behavior. Since every

<sup>1</sup> Ztschr. f. Elektrochemie 2, 497 (1896).

<sup>2</sup> Chem. Ztg. 22, 297 (1898).

<sup>3</sup> Proceed. Chem. Soc. 19, 58 (1903).

<sup>4</sup> D. R. P. No. 92007 (1895).

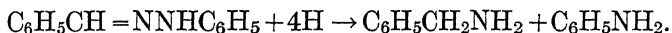
electrolytic cell performs both functions at both electrodes, the problem presents itself to apply both of these effects of the current to one and the same substance. We shall see that this possibility has actually been realized in individual cases.

**Salicin**, saligenin-glucose, by the action of the enzymes ptyalin and emulsion, is known to split up into glucose and saligenin (i.e. o-oxybenzyl, e.g. salicyl alcohol). On boiling with dilute acids the same decomposition occurs, but saligenin is resinified to saliretin. Tichanowitz<sup>1</sup> and Hostmann<sup>2</sup> found that salicin on electrolysis splits up into glucose and salicyl alcohol, the latter being partially oxidized to salicylic aldehyde and salicylic acid.

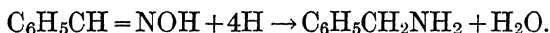
**Benzaldehyde**.—Kauffmann,<sup>3</sup> by electrolyzing benzaldehyde in a 12–15% solution of potassium bisulphite, obtained at the cathode a mixture of hydrobenzoin and isohydrobenzoin. According to his statements,<sup>4</sup> an alcoholic solution of sodium hydroxide is more suitable for the reaction than the aqueous solution of bisulphite. Other aldehydes and ketones show a behavior similar to that of benzaldehyde, as will be explained under the individual substances.

Tafel and Pfeffermann<sup>5</sup> have discovered a useful method for preparing amines. They electrolytically reduce oximes and phenylhydrazones in sulphuric-acid solution. Thus

*Benzylidenephénylhydrazone*, the condensation product of benzaldehyde and phenylhydrazine, gives 43 per cent. of the theoretical yield of benzylamine, besides some aniline:



*Benzaldoxime*, by reduction, is split up, yielding 69 per cent. of the theoretically possible quantity of benzylamine:



<sup>1</sup> Chem. Centralb. 613 (1861).

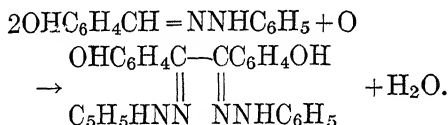
<sup>2</sup> Chem. Ztg. 17, 1099 (1893).

<sup>3</sup> Ztschr. f. Elektrochemie 2, 365 (1895)

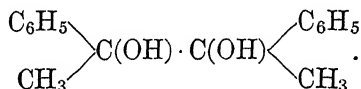
<sup>4</sup> Ibid. 4, 461 (1898).

<sup>5</sup> Ber. d. deutsch. chem. Gesellsch. 35, 1510 (1902).

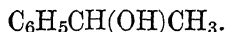
Salicylaldehydephenylhydrazone, by electrolytical oxidation in alkaline solution at a platinum anode can be converted into salicyl- $\alpha$ -osazone (Biltz <sup>1</sup>).



**Acetophenone**,  $\text{C}_6\text{H}_5 \cdot \text{CO} \cdot \text{CH}_3$ .—Acetophenone yields acetophenonepinacone,

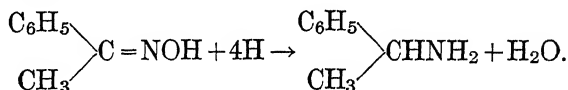


if reduced in alcoholic sodium hydroxide (Kauffmann <sup>2</sup>). Elbs and Brand <sup>3</sup> employed an alcoholic-alkaline solution and lead cathodes; electrolyzing at the boiling temperature, they also obtained acetophenonepinacone and a moderate yield of methylphenyl carbinol:



In sulphuric-acid solution and at lead cathodes the same substances are produced in almost equal yields.

*Acetophenoneoxime*, investigated by Tafel and Pfeffermann <sup>4</sup> in the same way as benzaldoxime, gives phenylethylamine sulphate:



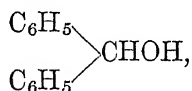
**Benzophenone**, on being reduced in alkaline solution at lead cathodes (Elbs and Brand <sup>5</sup>), gives benzhydrol almost quantitatively,

<sup>1</sup> Lieb. Am. 305, 167 (1899).

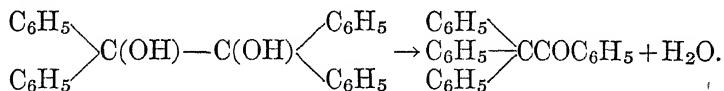
<sup>2</sup> Ztschr. f. Elektrochemie 4, 461 (1898).

<sup>3</sup> Ibid. 8, 784 (1902).

<sup>4</sup> l.

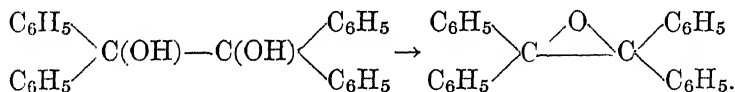


while in sulphuric-acid solution the reduction becomes more complicated. If the warm solution is electrolyzed with a moderate current density, there occurs as chief product  $\beta$ -benzpinacolone, which is to be regarded as a molecular rearrangement product of the primarily formed benzophenonepinacolone with splitting off of water:

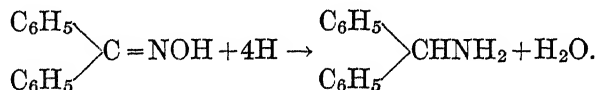


With a very small current density and at a low temperature ( $0^\circ$ – $2^\circ$ ) the yield of  $\beta$ -benzpinacolone is trifling, benzhydrol and diphenylmethane being chiefly produced.

If the alcohol and sulphuric acid are replaced by acetone and phosphoric acid respectively, and the electrolysis is carried out with a high current density and with a warm solution, there will be formed, by the action of phosphoric acid with simultaneous splitting off of water,  $\alpha$ -benzpinacolone, the rearrangement product of benzophenonepinacolone:



*Benzophenoneoxime.*—This substance, on electrolysis in a 60% sulphuric acid at lead and mercury electrodes—the latter being preferred on account of the difficultly soluble sulphate which is formed—is reduced to benzhydrylamine (Tafel and Pfeffermann<sup>1</sup>):



Elbs and Brand<sup>2</sup> also investigated the following ketones:

<sup>1</sup> l. c.

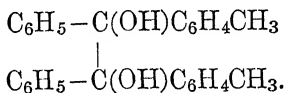
<sup>2</sup> l. c.



Phenyl-p-tolylketone, by alkaline reduction, gives almost quantitatively phenyl-p-tolylcarbinol:

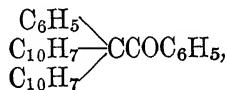


The same product, together with phenyl-p-tolylpinacone, is produced in sulphuric-acid solution at a low current density and temperature. With a higher current density and temperature the formation of carbinol is trifling, and a good yield of phenyltolylpinacone is obtained:



**Phenyl-m-xylylketone.**—The reaction product of the alkaline reduction is a liquid modification of phenyl-m-xylylcarbinol; but in sulphuric-acid-acetone solution at the boiling temperature phenyl-m-xylylpinacone is obtained. The yield of the latter is 40–50 per cent. of that theoretically possible.

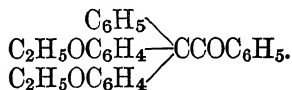
**Phenyl- $\alpha$ -naphthylketone.**—A satisfactory yield of phenyl- $\alpha$ -naphthylcarbinol is obtained in alkaline electrolytes; in acid solution only phenyl- $\alpha$ -naphthyl- $\beta$ -pinacolone,



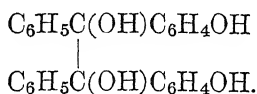
results. This is due to the fact that phenylnaphthylpinacone is very sensitive towards acids; thus only its conversion product is obtained above.

The same is true in acid solution of

**p-Ethoxybenzophenone**, which yields p-ethoxybenz- $\beta$ -pinacolone:



**p-Oxybenzophenone.**—While this ketone is not reducible in alkaline electrolytes, the normal reduction product, p-oxybenzopinacone, is produced in alcoholic-sulphuric acid:



**p-Oxybenzophenonebenzoate.**—This substance is reduced to the carbinol in sodium-acetate solution. To prevent saponification during reduction, the free alkali must be continually neutralized with acetic acid.

**Phthalyl-p-aminobenzophenone.**—This compound, by reduction in sulphuric-acid solution, gives a poor yield of pinacone.

Elbs and Brand sum up the results of their investigation as follows:

1. The electrochemical reduction of ketones in alkaline solution at lead cathodes gives the same products as the chemical reduction with sodium amalgam or with zinc dust and alkali; the process is in many cases suitable for the preparation of benzhydrols.

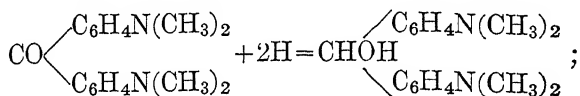
2. The electrochemical reduction of ketones in acid solution (dilute sulphuric or phosphoric acid) at lead cathodes leads to pinacones; if these are sensitive towards acids, the corresponding  $\alpha$  or  $\beta$  pinacolines are obtained in their stead. For this reason the electrochemical process is not so generally applicable for the preparation of aromatic pinacones as the method employing glacial acetic acid and zinc dust, which has been worked out by Elbs and Schmidt;<sup>1</sup> but the electrochemical reduction is more energetic than that with zinc dust and glacial acetic acid. Fatty ketones are reduced like the aromatic ketones, with the difference that fatty and fatty-aromatic ketones give simultaneously alcohols and pinacones, whereas pure aromatic ketones yield chiefly only pinacones.

**Tetramethyldiamidobenzophenone**, Michler's ketone, according to Kauffmann,<sup>2</sup> when electrolytically reduced in alcoholic

<sup>1</sup> Journ. f. prakt. Chem. **51**, 591 (1895).

<sup>2</sup> Ztschr. f. Elektrochemie **4**, 461 (1898).

sodium-hydroxide solution, gives the corresponding benzhydrol:

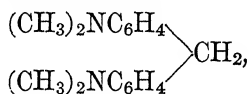


Elbs and Brand<sup>1</sup> obtained the same result.

Escherich and Moest<sup>2</sup> made an extensive investigation with the object of preparing electrolytically tetra-alkylated diamido-benzhydrols. They discovered that, by observing certain experimental conditions, the reduction can at will be directed to the hydrol or the pinacone. This is particularly true with Michler's ketone. We can thus obtain chiefly pinacone, for instance, by employing copper cathodes in a dilute sulphuric-acid solution; nickel cathodes, under the same conditions, yield about equal quantities of pinacone and hydrol, while by using lead cathodes and mercury cathodes, hydrol is chiefly produced. Moreover, the pinacone reaction occurs the more easily the more concentrated the solution is of the acid. Because of the resistibility of the resulting reduction products towards anodic oxygen, separate electrode chambers are not required.

Since

**Tetramethyldiamidodiphenylmethane,**



on electrolytic oxidation in dilute sulphuric acid at a lead anode also readily yields the hydrol, the oxidizing action of the current can also be employed, besides the reducing action, in the preparation of the hydrol, if a mixture of tetramethyldiamidodiphenylmethane and tetramethyldiamidobenzophenone in molecular proportion is electrolyzed. Escherich and Moest actually obtained a very good yield of the hydrol, —without an evolution of gas,—at the cathode and anode.

**Dibenzylketone.**—Elbs and Brand<sup>3</sup> have published a short

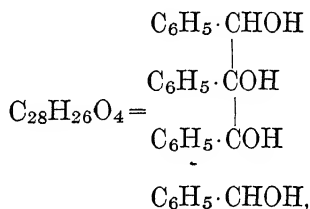
<sup>1</sup> Ztschr. f. Elektrochemie 8, 786 (1902).

<sup>2</sup> Ibid. 8, 849 (1902); D. R. P. No. 133896 (1901).

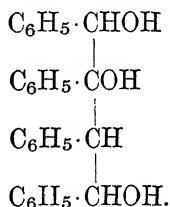
<sup>3</sup> Ztschr. f. Elektrochemie 8, 784 (1902).

note on this substance. The reduction seems to take place like that of other ketones; but the nature of the oily reaction-product was not determined.

**Benzile.**—The aromatic diketone benzile,  $\text{C}_6\text{H}_5\text{CO}\cdot\text{CO}\cdot\text{C}_6\text{H}_5$ , gives peculiar results (Kauffmann<sup>1</sup>). By reduction in an alkaline alcoholic solution a whole series of bodies is formed, i.e., benzoic acid, benzilic acid, tetraphenylerythrite:



and a substance,  $\text{C}_{28}\text{H}_{26}\text{O}_3$ , containing one less atom of oxygen, which has probably the constitution



Tetraphenylerythrite is also formed by the direct reduction of benzoin.

**Benzoin.**—Benzile, by reduction in dilute alcoholic sodium hydroxide and in alcoholic sulphuric acid, according to James,<sup>2</sup> can inversely be converted into benzoin. Oxidation of benzoin in alkaline and sulphuric-acid solution gives a poor yield of benzoic acid. In alcoholic hydrochloric acid, especially at a high current density, benzile is formed.

**Anthraquinone.**—The first researches concerning the electrolysis of this substance were made by Goppelsröder (see p. 194), who, by suspending anthraquinone in potassium hydroxide,

<sup>1</sup> Ztschr. f. Elektrochemie **4**, 461 (1898).

<sup>2</sup> Journ. Am. Chem. Soc. **21**, 889 (1899).

suspected reduction products, such as oxyanthranol or hydroanthroquinone, among the substances deposited on the cathode electrode. If the current is sent through a mixture of anthraquinone and molten alkali, oxyanthraquinone first, then alizarate, and then purpurate, is supposed to be formed. These experiments, however, require to be repeated with greater exactitude.

According to Weizmann,<sup>1</sup> anthraquinone, dissolved in concentrated sulphuric acid, is converted by electrolytic oxidation into monoxy-, dioxy-, and trioxyanthraquinone. An addition of oxalic acid to the sulphuric acid is suitable for obtaining dioxyanthraquinone. A nitrooxyanthraquinone, which is convertible by electrical reduction into amidoalizarin, is similarly obtained from *mononitroanthraquinone*.<sup>2</sup> The amidoalizarin can be directly obtained from nitroanthraquinone if its solution is electrolyzed with an alternating current. The sulphonic-acid derivatives of anthraquinone behave like anthraquinone.

The phenomena occurring with these oxidations were later more accurately investigated by Perlin.<sup>3</sup> From anthraquinone in 92% sulphuric acid 90 to 96% dioxyanthraquinones and a small quantity of monoanthraquinones were obtained. Besides  $\alpha$ - and  $\beta$ -monooxanthraquinone, quinizarin, alizarin, and purpurin could be isolated. If the anthraquinone-sulphuric acid solution is employed as cathode fluid, anthranols, anthrones, and hydroanthranols are formed. If the sulphuric-acid concentration of the anode solution is increased, there are formed sulphurated oxyanthraquinones.

*$\alpha$ -Mononitroanthraquinone*, under like conditions, gives a nitrooxyanthraquinone besides a mixture of di- and trioxyanthraquinone.

*Dibromanthraquinone* gives violet crystals, perhaps a tetraoxydibromanthraquinone.

**Phenanthrenequinone**, according to Perlin, is electrolytically oxidized in concentrated sulphuric-acid solution to a mixture of mono- and trioxyphenanthrenequinone.

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<sup>1</sup> F. P. No. 265291 (1897).

<sup>2</sup> F. P. No. 265292 (1897).

<sup>3</sup> Diss. Berlin, March, 1899.

All these oxidation processes illustrate the possibility already mentioned (p. 132) of introducing oxygen electrolytically into the benzene nucleus.

## 6. ACIDS.

The electrolysis of aromatic acids by no means offers results which are comparable to those obtained by the electrolysis of aliphatic acids. In so far as the aromatic acids, or their salts, act as electrolytes, a regeneration of the acid from the anion  $\text{RCOO}^-$  and water, with evolution of oxygen, occurs almost exclusively. A splitting off of carbonic acid, which makes possible the manifold reactions of aliphatic acids, almost never occurs here. The results obtained with aromatic acids are, therefore, only of a more general interest so far as the acids, by substitutions in the benzene nucleus, can act as cathodic or anodic depolarizers, and can in this way exert reduction and oxidation effects.

**Benzoic Acid.**—Benzoic acid and its salts were examined by several investigators, first by Matteucci,<sup>1</sup> then by Brester,<sup>2</sup> but most thoroughly by Bourgoin.<sup>3</sup>

The result of all these investigations is to show that here no secondary reactions take place, as was observed in the case of the fatty acids, but that the only effect of the current is to produce a separation into hydrogen (or metal) and the acid radical, the latter regenerating the acid at the positive pole.

In an alkaline solution it is possible to so increase the oxidation that the benzoic acid is destroyed. The decomposition products which then appear at the anode are carbon dioxide, carbon monoxide, and sometimes acetylene. The odor of bitter almonds is also frequently observed.

A thorough investigation was made by Löb,<sup>4</sup> who employed a current having a potential of 6–7 volts and a current density of 15–20 amp. per sq. cm. and obtained a small quantity of

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<sup>1</sup> Bull. soc. chim. 10, 209 (1868).

<sup>2</sup> Jahresb. f. Chem. (1866), 87.

<sup>3</sup> Bull. soc. chim. 9, 431 (1867).

<sup>4</sup> Ztschr. f. Elektrochemie, 2, 663; 3, 3 (1896).

a substance containing sodium, but the chemical nature of which has not yet been determined. There is formed besides this compound a small quantity of benzaldehyde, as well as acetylene and carbon monoxide. Under no circumstances do diphenyl or other hydrocarbons occur; nor do fatty acids appear, which is otherwise generally the case in an extensive oxidation of this character.

According to the investigations of Schall,<sup>1</sup> diphenyl does, however, occur if a solution of sodium benzoate in molten benzoic acid is electrolyzed at 100 volts between silver electrodes.

*Benzoic Esters.*—Tafel and Friedrichs,<sup>2</sup> by conducting the electrolysis in alcoholic-aqueous sulphuric acid at lead or mercury cathodes, obtained methyl benzyl ether and the ethyl benzyl ether from benzoic methyl and benzoic ethyl esters respectively. Mettler,<sup>3</sup> by a similar arrangement, obtained chiefly benzyl alcohol and some benzyl methyl ether from benzoic methyl ester.

The *esters of monochlor- and brombenzoic acids* also yield the corresponding ethers and alcohols.

**Thiobenzoic Acid.**—On electrolyzing this acid Bunge<sup>4</sup> obtained the bisulphide of benzoyl.

**Sulphobenzoic Acid.**—This acid, according to the statements of the same investigator, is not changed by the current.

**Phthalic Acid.**—Bourgoin<sup>5</sup> states that the electrolysis of this acid and of its neutral or alkaline salts resulted in the formation of the unchanged acid at the positive pole. The appearance of small quantities of carbon dioxide and carbon monoxide, however, was an evidence that a small portion of the acid had undergone oxidation.

The potassium salt of the mono-ethyl ester of phthalic acid, when electrolyzed by Brown and Walker,<sup>6</sup> became dark-colored, and a resinous substance was formed, but the isolation of any

<sup>1</sup> Ztschr. f. Elektrochemie 6, 102 (1899).

<sup>2</sup> Ber. d. deutsch. chem. Gesellsch. 37, 3182 (1904).

<sup>3</sup> Ibid. 37, 3692 (1904).

<sup>4</sup> Ibid. 3, 296 (1870).

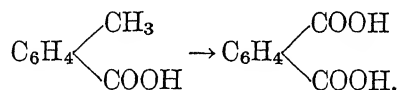
<sup>5</sup> Jahresb. f. Chem. 631 (1871).

<sup>6</sup> Lieb. Ann. 274, 67 (1893).

new electrolytic product was not possible. *Phthalic esters*, according to Tafel and Friedrichs,<sup>1</sup> can be readily reduced in the presence of sulphuric acid at lead or mercury cathodes.

**Phenylacetic Acid.**—This acid, electrolyzed in the form of its potassium salt by Slawik,<sup>2</sup> yielded free phenylacetic acid.

**p-Toluic Acid.**—According to an incomplete research by Labhardt and Zschoche,<sup>3</sup> p-toluic acid in alkaline solution at polished platinum anodes is oxidized to terephthalic acid:



**p-Toluenesulphonic Acid.**—This acid gives at platinum and lead electrodes a poor yield of p-sulphobenzoic acid (Sebor<sup>4</sup>).

**Cinnamic Acid.**—Cinnamic acid, investigated by Brester,<sup>5</sup> showed a similar behavior in the electrolysis of both the free acid and the neutral solutions of its salts. Löb<sup>6</sup> has reported an accidental observation on the formation of *bromstyrene* by electrolysis of cinnamic acid in the presence of potassium bromide.

In acid solution Marie<sup>7</sup> converted cinnamic acid almost quantitatively into hydrocinnamic acid.

**Benzylmalonic Acid.**—When this acid in the form of its ethyl-potassium salt was submitted to electrolysis by Brown and Walker<sup>8</sup> it exhibited a behavior materially different from that of malonic acid. The solution became dark-colored, but contained no new compound. If oxidation occurred, it was a complete oxidation into carbon dioxide and carbon monoxide, such as has been observed in the case of unsaturated acids.

However, when v. Miller<sup>9</sup> electrolyzed the ethyl-potassium

<sup>1</sup> l. c.

<sup>2</sup> Ber. d. deutsch. chem. Gesellsch. **7**, 1051 (1874).

<sup>3</sup> Ztschr. f. Elektrochemie **8**, 93 (1902).

<sup>4</sup> Ibid. **9**, 370 (1903).

<sup>5</sup> Jahresb. f. Chem. **87** (1866).

<sup>6</sup> Ztschr. f. Elektrochemie **3**, 46 (1896).

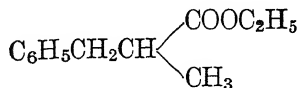
<sup>7</sup> Compt. rend. **136**, 1331 (1903).

<sup>8</sup> Lieb. Ann. **274**, 67 (1893).

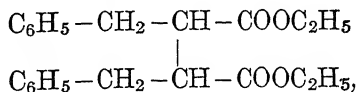
<sup>9</sup> Ztschr. f. Elektrochemie **4**, 57 (1897).



salt of this acid in the presence of *potassium acetate*, not only  $\alpha$ -methylhydrocinnamic ester,



but also dibenzylsuccinic ester,



was produced, as was to be expected according to the Brown-Walker reaction. There are also present the normal by-products of the electrolysis of such kind of acids, in this case hydrocinnamic acid and cinnamic acid. On repeating these experiments, Hauser<sup>1</sup> was also able to isolate propylbenzene, the formation of which was brought about by the electrolysis of hydrocinnamic ester—readily formed from the material started with—and potassium acetate.

The electrolysis of the ester-salt of benzylmalonic acid with *potassium butyrate* and *caproate* takes place just as with potassium acetate. Good yields of propylhydrocinnamic ester and amylhydrocinnamic ester, besides dibenzylsuccinic ester and cinnamic and hydrocinnamic esters, are obtained.

**Dibenzylacetic Acid.**—This substance, on electrolysis of its potassium salt, and a mixture of this salt with fatty acid salts, gives no tangible products.

**Salicylic Acid.**—The formation of yellow mordant dyes, which are obtained by the electrolytic oxidation of aromatic oxycarboxylic acids in sulphuric-acid solution (Badische Anilin- u. Sodafabrik<sup>2</sup>), seems to be based on the frequently mentioned introduction of oxygen into the benzene nucleus. The materials serving as starting-point, aside from salicylic acid, were symmetrical *m*-dioxibenzoic acid, *gallic acid*, *tannin*, *gallaminic acid*, *esters of the acids*, *m*- and *p*-oxybenzoic acid, and other oxy-acids.

<sup>1</sup> Dissertation Munich (1901).

<sup>2</sup> D. R. P. No. 85390 (1895).

The electrolytic introduction of halogens into salicylic acid has been mentioned under phenols (p. 201).

Von Miller and Hofer<sup>1</sup> have applied their method for the electrolysis of organic oxy-acids to several aromatic acids containing substituents; these experiments may briefly be mentioned here.

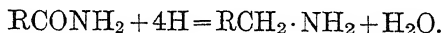
**Phenyl- $\beta$ -lactic Acid.**—This acid gives at the anode benzaldehyde, besides resinous bodies.

**Mandelic Acid.**—This substance yielded at the anode chiefly carbonic acid, a little carbon monoxide, and also benzaldehyde. The same body was formed in the electrolysis of *phenyl-glyceric acid*.

**Sulphoanthranilic Acid.**—This substance, according to a patent<sup>2</sup> of Kalle & Co., can be converted into anthranilic acid if electrolyzed in neutral or slightly acid solution at a mercury cathode.

#### 7. ACID AMIDES AND NITRILES.

According to the investigations of Baillie and Tafel,<sup>3</sup> the reduction of acid amides in sulphuric-acid solution at lead cathodes leads to amines, as shown in the equation:



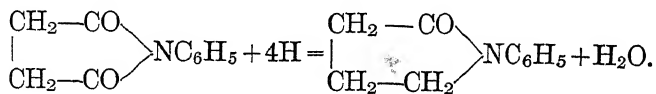
**Benzamide** yields only a little benzylamine; benzaldehyde, which probably contained benzyl alcohol, was also formed. In a similar manner

**Dimethylbenzamide** gives dimethylbenzylamine;

**Acetanilide** gives ethylaniline;

**Acetyl-o-toluidine** gives ethyl-o-toluidine; and

**Succinanil** gives phenylpyrrolidone:



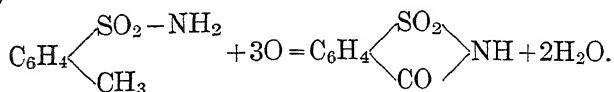
<sup>1</sup> Ber. d. deutsch. chem. Gesellsch. **27**, 461 (1894).

<sup>2</sup> D. R. P. No. 146716 (1902).

<sup>3</sup> Ber. d. deutsch. chem. Gesellsch. **32**, 63 (1899).

(The same reaction in the aliphatic series, p. 119, in the pyridine and quinoline series, p. 218.)

**o-Toluenesulphonamide** (o-Toluenesulphamide).—According to a patent of F. v. Heyden Nachfolger,<sup>1</sup> benzoylsulphonimides can be prepared by the electrolytic oxidation of toluenesulphonamides in alkaline, or earthy-alkaline solution; for example, o-benzoylsulphonimide (benzoic sulphimide), or saccharin, from o-toluenesulphonamide:



The p-nitro-substitution products of o-toluenesulphonamide are said to behave similarly.

Just as amines are easily obtained by reduction of nitriles with sodium amalgam or sodium and alcohol, so this reaction can be carried out electrolytically (p. 121).

**Benzonitrile**.—Ahrens,<sup>2</sup> by electrolytic reduction of this substance in dilute sulphuric acid at a platinum cathode, obtained benzylamine; in like manner,

**Benzylcyanide** gave the corresponding phenylethylamine.

## 8. THE INDIGO REDUCTION.

The reduction of indigo by electrolytic hydrogen in alkaline suspension, the fluid being warmed, has already been carried out by Fr. Goppelsröder<sup>3</sup> and v. Wartha.<sup>4</sup> Mullerus<sup>5</sup> easily reduced indigosulphonic acid.

Thorough studies regarding the process of the reduction of indigo by the electric current have recently been made by A. Binz,<sup>6</sup> and Binz and Hagenbach<sup>7</sup>; these show that most probably zinc and not hydrogen plays the chief part in the reduction. Thus when indigo is electrolytically reduced in

<sup>1</sup> D. R. P. No. 85491 (1895).

<sup>2</sup> Ztschr. f. Elektrochemie **3**, 100 (1896).

<sup>3</sup> Preparation and Fixation of Dyes with the Aid of Electrolysis, Reichenberg, 1885.

<sup>4</sup> Chem. Ztg. **8**, No. 25 (1884).

<sup>5</sup> Ibid. **17**, 1454 (1893).

<sup>6</sup> Ztschr. f. Elektrochemie **5**, 5, 103 (1898); **9**, 599 (1903).

<sup>7</sup> Ibid. **6**, 261 (1899).

alkaline solution, almost no formation of indigo-white occurs, but if alkaline-zinc solutions and zinc cathodes are employed a smooth reduction (formation of the vat) takes place.

Binz concludes further that the conversion of indigo into indigo-white depends upon a withdrawal of oxygen and not upon the taking up of hydrogen, as hitherto supposed. The phenomena observed in the reduction of indigo agree with the views regarding the behavior of attackable cathodes, as mentioned in the introduction (p. 18). The reducing agent is the discharged zinc-ions, whose separation on the cathode and whose reaction with the depolarizer indigo occurs in a proportion which depends upon the velocities of the two processes. The cathode potential appears as a measure for the reduction energy, whose value is naturally determined by the chemical nature of the zinc, and cannot forthwith be attainable by any other reducing agent such as hydrogen. In this respect we can say with Binz that the indigo reduction is based upon the direct action of the metal.

Without entering upon the subject of the electrolytic preparation of reducing substances which are useful for vat formation, such as hydrosulphites, a process<sup>1</sup> of the Farbwerke Meister, Lucius and Brüning in Höchst may here be mentioned by which sulphite solutions are electrolyzed at higher temperatures in the presence of indigo. Hereby the sulphites are converted into hydrosulphites, which accomplish the reduction of indigo, the sulphites being regenerated. The latter are again continually reduced. In alkaline electrolytes a vat is immediately formed and in acid solutions solid indigo-white is precipitated. The current density and cathode material can at will be chosen within wider limits.

#### 9. PYRIDINE DERIVATIVES AND ALKALOIDS.

The pyridine ring is easily reducible. Hydropyridines are formed from pyridine and its derivatives, and piperidines by complete hydration. Quinoline and acridine are also easily converted into hydro-compounds.

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<sup>1</sup> D. R. P. No. 139567 (1902).

These reductions can easily be obtained with the electric current under suitable conditions; the alkaloids, which have a pyridine nucleus, also behave analogously.

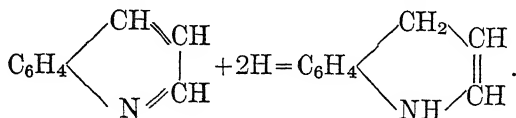
**Pyridine.**—Ahrens<sup>1</sup> accomplished the electrolytic reduction of *pyridine* and the derivatives of pyridine, and obtained piperidine from pyridine, and  $\alpha$ -pipecoline from  $\alpha$ -*picoline*. In these electrolyses lead cathodes and 10% solutions of sulphuric acid were employed.

If strong sulphuric acid and a platinum cathode are used there is formed a substance containing nitrogen and sulphur, the chemical nature of which has not yet been determined.

**Benzoylpiperidine.**—On the occasion of their experiments regarding the reduction of acid amides, Baillie and Tafel,<sup>2</sup> by electrolytical reduction in sulphuric acid at a lead cathode, converted benzoylpiperidine into benzylpiperidine and obtained a yield of 77 per cent. of the latter compound.

**Quinoline** was electrolyzed by Ahrens<sup>3</sup> in a 10% sulphuric acid. The cathode was of lead, and the anode of platinum. An apparently tri-molecular hydroquinone ( $C_9H_9N$ )<sub>3</sub> was chiefly formed at the cathode, besides small quantities of hydroquinoline ( $C_9H_9N$ )<sub>2</sub> and tetrahydroquinoline,  $C_9H_{11}N_2$ .

According to a later patent of E. Merck,<sup>4</sup> if quinoline is electrolyzed in dilute sulphuric acid containing for 1 equivalent of the base at least 4 equivalents of the acid, and free from metallic salts, a good yield of dihydroquinoline is obtained.



**Acetyltetrahydroquinoline.**—As in the case of benzoylpiperidine, Baillie and Tafel<sup>5</sup> were able to reduce this compound, and obtained a good yield of ethyltetrahydroquinoline.

<sup>1</sup> Ztschr. f. Elektrochemie **2**, 577, 580 (1896); also D. R. P. No. 90308 (1896).

<sup>2</sup> Ber. d. deutsch. chem. Gesellsch. **32**, 74 (1899).

<sup>3</sup> Ztschr. f. Elektrochemie **2**, 580 (1893).

<sup>4</sup> D. R. P. No. 104664 (1898).

<sup>5</sup> Ber. d. deutsch. chem. Gesellsch. **32**, 74 (1899).

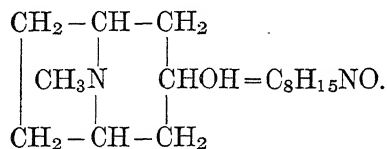
**Quinaldine** ( $\alpha$ -methylquinoline), according to the process of Ahrens,<sup>1</sup> can be converted into dihydroquinaldine,  $C_{10}H_{10}NH$ , and tetrahydroquinaldine,  $C_{10}H_{13}N$ .

The nitroso- and nitro-derivatives of the pyridine and quinoline series have already been discussed (see p. 192).

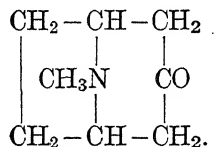
The *coca-alkaloids*, like cocaine, atropine, etc., contain perhaps a combination of a piperidine ring with a pyrrolidine ring. This combination is also expressed in their behavior in electrolysis. At present the following is known.

**Atropine**,  $C_{17}H_{23}NO_3$ .—From the neutral sulphate of atropine crystallized atropine is gradually precipitated at the cathode, while at the anode carbon dioxide, carbon monoxide, oxygen, and nitrogen are evolved. The acid sulphate behaves in a similar manner, but the evolution of nitrogen was not observed (Bourgoin<sup>2</sup>).

Atropine is decomposed by baryta water into tropic acid and **Tropine**.



This substance, on electrolysis in alkaline and acid solution at lead electrodes, and at a low temperature, is converted into tropinone.<sup>3</sup>



A good yield of this substance is obtained. *Pseudotropine* behaves in the same manner.

<sup>1</sup> Ztschr. f. Elektrochemie **2**, 580 (1896).

<sup>2</sup> Bull. soc. chim. **12**, 400 (1869).

<sup>3</sup> D. R. D. No. 118607 (1900).

**Tropinone.**—This compound can inversely be easily reduced to pure tropine. The chem. Fabrik vorm. E. Schering<sup>1</sup> employs as electrolyte an aqueous ammoniacal ammonium sulphate solution.

E. Merck,<sup>2</sup> by electrolysis of a slightly alkaline solution, obtains, besides tropine, pseudotropine. The yield is 50 per cent. of the tropinone employed.

### Opium Bases.

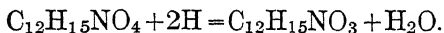
**Opium.**—If opium is subjected to the action of the electric current, morphine ( $C_{17}H_{19}NO(OH)_2$ ) goes to the cathode and meconic acid (oxypyronedicarboxylic acid) to the anode (Lassaigne).<sup>3</sup>

**Morphine**,  $C_{17}H_{19}NO_3 + H_2O$ .—Pommerehne,<sup>4</sup> by the electrolysis of a solution of morphine acidified with sulphuric acid, obtained after a few days crystals of oxydimorphine sulphate at the anode. The solution became dark-colored.

**Codeïne** (methyilmorphine)  $C_{17}H_{17}NO(OH)O \cdot CH_3$ . — On electrolysis of the neutral sulphate hydrogen is evolved, codeïne is precipitated, and the solution turns brown (Bourgoin<sup>5</sup>).

The acid sulphate undergoes more complete decomposition, and carbon dioxide, carbon monoxide, oxygen, and nitrogen are split off.

**Cotarnine**,  $C_{12}H_{15}NO_4$  — This compound is converted quantitatively by the electrolytic hydrogen into pure hydrocotarnine (Brandon and Wolfenstein<sup>6</sup>):



**Hydrastinine**,  $C_{11}H_{13}NO_3$ , which does not, indeed, belong to the opium bases, may nevertheless be mentioned here. This substance is similarly converted into hydrohydrastinine,  $C_{11}H_{13}NO_2$ .

<sup>1</sup> D. R. D. No. 96362 (1898).

<sup>2</sup> D. R. D. No. 115517 (1900).

<sup>3</sup> Tommasi, *Traité d'Electrochimie* 788 (1889).

<sup>4</sup> Arch. Pharm. **235**, 364 (1897).

<sup>5</sup> Bull. soc. chim. **12**, 400 (1869).

<sup>6</sup> Ber. d. deutsch. chem. Gesellsch. **31**, 1577 (1898); D. R. P. No. 94949 (1897).

## Quina- and Strychnos Bases.

**Quinine**,  $C_{20}H_{24}N_2O_2$ .—Although the neutral sulphate is a very poor conductor, the acid sulphate is readily decomposed into carbon dioxide, carbon monoxide, and nitrogen. The color of the solution changes to a dark brown.

Besides the last-named gases, the above-mentioned alkaloids split off various other products, principally complicated nitrogen-containing compounds (Bourgoin <sup>1</sup>).

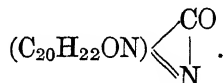
Pommerehne,<sup>2</sup> by electrolysis of a sulphuric-acid quinine solution, obtained a green resinous mass, which is perhaps identical with thalleioquin (?).

*Quinine*, *cinchonine* ( $C_{19}H_{22}N_2O$ ), and *cinchonidine* ( $C_{19}H_{22}N_2O$ ), on electrolysis at lead cathodes in a 50% sulphuric-acid solution, are converted into non-crystallizable tetrahydro-bodies (Tafel and Naumann <sup>3</sup>).

**Strychnine**,  $C_{21}H_{22}N_2O_2$ .—The neutral sulphate suffers but little change. The solution becomes slightly colored, hydrogen and oxygen are given off, and crystals of strychnine collect at the cathode.

The acid sulphate behaves in a like manner, except that in its case the formation of carbon dioxide and carbon monoxide, as well as oxygen and nitrogen, shows that a part of the substance undergoes complete decomposition. In strongly acid solutions the splitting off of nitrogen does not occur (Bourgoin <sup>4</sup>).

Tafel and Naumann <sup>5</sup> have made more thorough investigations regarding the electrolytic reduction of strychnine in strong sulphuric acid solution at lead cathodes. According to Tafel's researches, strychnine is to be regarded as a cyclical acid anilide of the formula:



<sup>1</sup> Bull. soc. chim. **12**, 400 (1869).

<sup>2</sup> l. c.

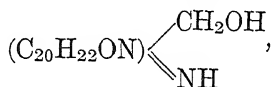
<sup>3</sup> Ber. d. deutsch. chem. Gesellsch. **34**, 3299 (1901).

<sup>4</sup> Bull. soc. chim. **12**, 400 (1869).

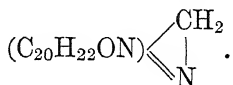
<sup>5</sup> Lieb. Ann. **301**, 291 (1898); Ber. d. deutsch. chem. Gesellsch. **34** 3291 (1901).



The water-soluble tetrahydrostrychnine is first formed:



which by further reduction is converted into strychnidine:



The quantity of the former preponderates at a low temperature. On the other hand, the higher the temperature the greater the quantity of strychnidine formed.

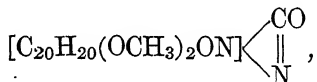
**Brucine**,  $\text{C}_{23}\text{H}_{26}\text{N}_2\text{O}_4$ .—A solution of the neutral sulphate turns red and the sulphate is decomposed. Hydrogen is evolved at the negative pole, but the brucine completely absorbs the oxygen at the positive pole (Bourgoin).

The acid salt is very energetically decomposed, becoming first red and then brown. At the anode carbonic-acid gas, carbon monoxide, oxygen, and nitrogen escape (Bourgoin<sup>1</sup>).

Besides the gases mentioned, the above alkaloids break up into other products, principally complex compounds containing nitrogen.

According to Tafel's and Naumann's<sup>2</sup> investigations, brucine behaves like strychnine in so far as that by reduction under similar conditions tetrahydrobrucine is produced; however, to obtain the crystalline product the temperature must not exceed 15°. But a body corresponding to strychnidine was not found among the products of the electrolytic reduction of brucine.

If we give brucine the following formula (Moufang and Tafel<sup>3</sup>):

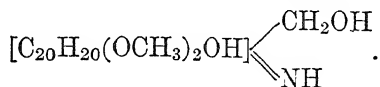


<sup>1</sup> l. c.

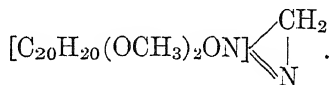
<sup>2</sup> l. c.

<sup>3</sup> Lieb. Am. 304, 24 (1898).

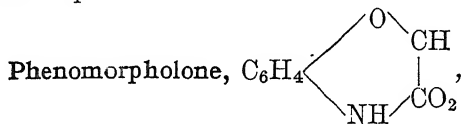
then tetrahydrobrucine has most probably the formula:



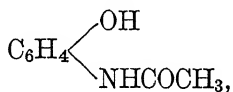
Brucidine, corresponding to strychnidine, is formed from tetrahydrobrucine if this is heated to  $200^\circ$ , water being split off:



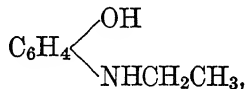
**Morpholone.**—Lees and Shedden<sup>1</sup> have investigated the electrolytic reduction of pheno- and naphthomorpholones in sulphuric-acid solution. Morpholines are produced only as by-products, the morpholone ring being for the most part broken up.



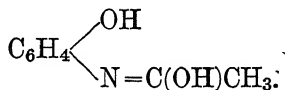
gives as end-products of the reduction acetyl-o-aminophenol,



also ethyl-o-aminophenol,

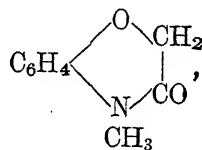


and also isoacetyl-o-aminophenol,

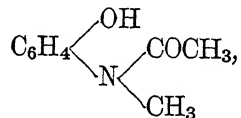


<sup>1</sup> Proceed. Chem. Soc. **19**, 132 (1903); Journ. Chem. Soc. **83**, 750 (1903)

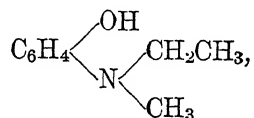
n-Methylphenomorpholone,



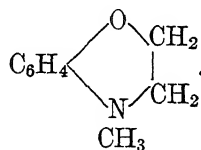
gives, besides n-acetylmethyl-o-aminophenol,



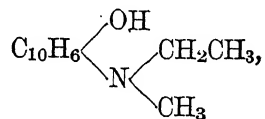
and n-methylethyl-o-aminophenol,



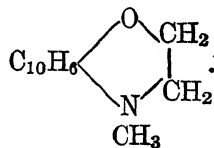
also n-methylphenomorpholine,



n-Methyl- $\beta$ -naphthomorpholone gives n-methylethyl- $\alpha$ -amino- $\beta$ -naphthol:

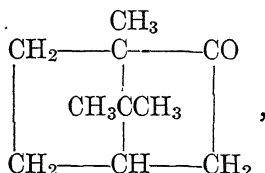


and n-methyl- $\beta$ -naphthomorpholine:

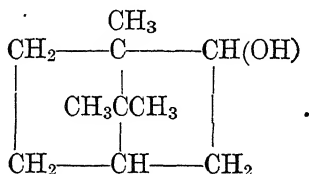


## 10. THE CAMPHOR GROUP.

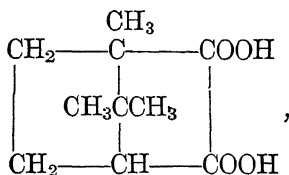
**Camphor.**—This substance, as shown by the synthesis carried out by Romppa,<sup>1</sup> has certainly the formula proposed by Bredt:



Being a ketone it can be reduced to the secondary alcohol borneol:



This reduction has been carried out electrolytically by Tafel and Schmitz<sup>2</sup> in sulphuric-acid solution at mercury cathodes. They obtain thus about 45 per cent. of the theoretically possible yield, with a maximum current consumption of 38 per cent. At lead cathodes no satisfactory reduction can be effected.

**Camphoric Acid,**

is the oxidation product of camphor with nitric acid.

Brown and Walker<sup>3</sup> also electrolyzed (see p. 102) the sodium-ethyl salt of camphoric acid and obtained two esters which they were able to separate by means of fractional dis-

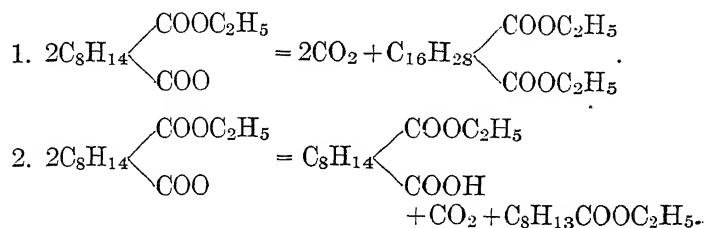
<sup>1</sup> Ber. d. deutsch. chem. Gesellsch. **36**, 4332 (1903).

<sup>2</sup> Ztschr. f. Elektrochemie **8**, 288 (1902).

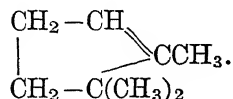
<sup>3</sup> Lieb. Ann. **274**, 71 (1893).

tillation. One of these (boiling-point  $212^{\circ}$ – $213^{\circ}$ ) on being saponified yielded an unsaturated monobasic acid,  $C_9H_{14}O_2$ , *campholytic acid*; the other having a higher boiling-point ( $240^{\circ}$ – $242^{\circ}$ ), was the neutral ester of a dibasic acid,  $C_{18}H_{30}O_4$ , to which Walker gave the name of *camphothetic acid*. These experiments are of great importance, because they prove the dibasic nature of camphoric acid, a fact which was doubted by Friedel.

Walker and Henderson<sup>1</sup> found, moreover, that upon electrolysis of concentrated aqueous solutions of the ethyl-potassium salt of *allocamphoric acid* there are formed as chief products the ethyl esters of a dibasic acid,  $C_{16}H_{28}(COOH)_2$ , and of a monobasic acid,  $C_8H_{13}COOH$ :



It has been found on further investigation<sup>2</sup> that besides the strongly dextrorotary unsaturated acid designated as *allocampholytic acid*,  $C_8H_{13}COOH$ , an isomeric acid is formed which, although slightly dextrorotary as obtained, is perhaps even lævorotary in an entirely pure condition. The latter on being heated to  $200^{\circ}$  splits off carbon dioxide and yields a hydrocarbon,  $C_8H_{14}$ , which boils at  $120$ – $122^{\circ}$  and appears to be identical with *laurolene*,



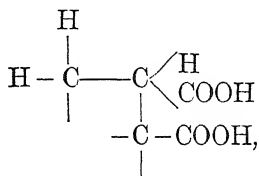
made from camphoric acid.

A ketonic acid,  $C_8H_{13}O \cdot COOH$ , melting-point  $228^{\circ}$ , is also found as an additional product of the electrolysis of potassium

<sup>1</sup> Journ. Chem. Soc. **67**, 337 (1895).

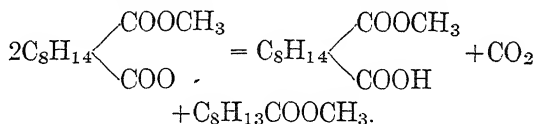
<sup>2</sup> Ibid. **69**, 748 (1897).

allocamphoric ethyl ester. The authors concluded from their observations that camphoric acid contains the group

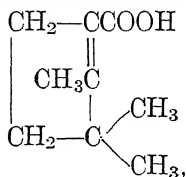


a deduction which had, of course, to be later modified.

According to later experiments of Walker and Cormack,<sup>1</sup> it is possible to obtain isolaunonic acid by electrolyzing the methyl-ester-potassium salt of camphoric acid:

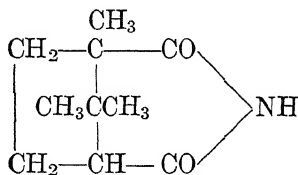


The free optically inactive isolaunonic acid,



was obtained from the latter ester. The electrolytic reaction occurs hence in a normal direction.

**Camphoric-acid imide,**



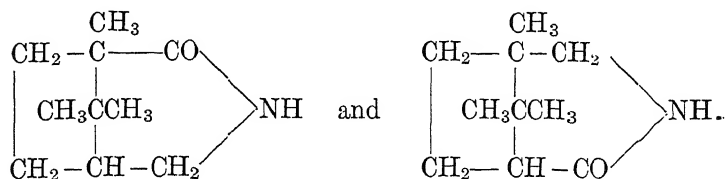
was reduced in sulphuric-acid solution at a prepared lead cathode. The experiment was made by Tafel and Eckstein,<sup>2</sup> in connection with their investigations concerning the electro-

<sup>1</sup> Proceed. Chem. Soc. **16**, 58 (1900).

<sup>2</sup> Ber. d. deutsch. chem. Gesellsch. **34**, 3274 (1901); see also D. R. P. No. 126196 (1900).

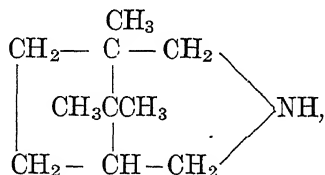
lytic reduction of succinimide (p. 119). Just as succinimide, by replacement of one of the two oxygen atoms by two hydrogen atoms, is converted into pyrrolidone and, by complete elimination of the oxygen, into pyrrolidine—although only to a very slight extent—so camphoric-acid imide gives two perfectly analogous products, camphidone and camphidine.

Camphidone occurs in two isomeric modifications, separable in the form of the picrates,  $\alpha$ -camphidone and  $\beta$ -camphidone:



Which one of these is the  $\alpha$ - and which the  $\beta$ -camphidone remains undecided.

Camphidine,



is always produced besides camphidones, and can be readily separated from these, since it possesses a decidedly basic character.

As the camphidones are extremely resistant towards further reduction, they form no intermediate phase in the camphidine formation. We must suppose that only those acid-imide molecules, both of whose carboxylic groups are by accident *simultaneously* attacked by the reducing agent, are changed into camphidine. Or, a carbinol-like intermediate product, in which the second carboxylic group—in contradistinction to that of camphidone—is electrolytically attackable, is already formed during the transition from camphoric-acid imide to the camphidone.

## 11. ELECTROLYSIS OF BLOOD AND ALBUMEN.

**Blood.**<sup>1</sup>—The defibrinated blood of a dog was submitted to electrolysis by Becquerel. He made use of platinum electrodes and a current furnished by a battery of three Daniell cells. At the negative pole he observed the following phenomena:

The blood became brown and alkaline, and contained neither white nor red corpuscles; it possessed the property of gradually dissolving blood-corpuscles and had the odor of putrid meat.

At the positive pole undecomposed and partially decomposed blood-corpuscles were present in large quantities. The fluid gave a precipitate of albumen with nitric acid, mercuric chloride and lead acetate.

**Albumen.**<sup>2</sup>—When an albumen solution was electrolyzed by Dumas and Prevost, under conditions similar to those used by Becquerel for blood, the alkali metal went to the negative pole, hydrogen was evolved, and acetic and phosphoric acids appeared at the positive pole. The result of this is that the albumen is coagulated at the negative pole (by the alkali present), while at the positive pole the solution remains clear.

As Lassaigne has shown, pure albumen in aqueous solution is a non-conductor of electricity; the addition of salts or acids is therefore necessary in its electrolysis.

The Pharmaceutical Institute of L. W. Gans of Frankfurt<sup>3</sup> has made known a process for electrochemically preparing fluorine-substitution products of albumens. The latter are suspended, or dissolved in a dilute aqueous solution of hydrofluoric acid or salts of this acid, and subjected at a platinum electrode to the anode current action. The discharged fluorine reacts with the albumen, forming substitution products.

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<sup>1</sup> Tommasi, *Traité d'Electrochimie* 800 (1889).

<sup>2</sup> l. c.

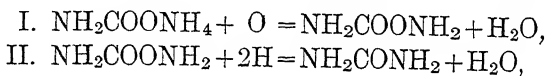
<sup>3</sup> D. R. P. No. 116881 (1898).



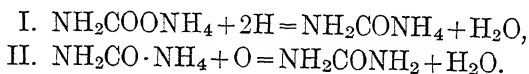
## CHAPTER V.

### ELECTROLYSIS WITH ALTERNATING CURRENTS.

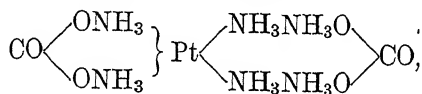
If the polarity of the current is not allowed to change too rapidly, it is possible, since oxidation and reduction occur successively at each pole, to accomplish electrolyses with alternating currents. Experiments with this end in view have been made by Drechsel.<sup>1</sup> Dehydration is a case of simultaneous reduction and oxidation. The supposition that in living organisms carbamide is produced from ammonium carbamate by the splitting off of water prompted Drechsel to make experiments in this direction. When an aqueous solution of ammonium carbamate is electrolyzed with a current from a battery of 4-6 Grove cells, and platinum electrodes used, carbamide is obtained independently of the electrode material when alternating currents are employed. The reactions are supposed to be either



or



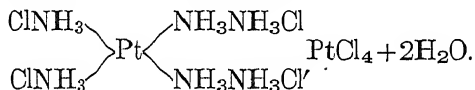
The observation that the platinum electrodes were strongly attacked, with the formation of platinum salts, caused Gerdes<sup>2</sup> to investigate the platinum bases. As the principal product he found a compound to which he gave the following formula:



<sup>1</sup> Journ. prakt. Chem. **22**, 476 (1880); Ber. d. deutsch. chem. Gesellsch. **13**, 2436 (1880).

<sup>2</sup> Journ. prakt. Chem. **26**, 257 (1882); see also Inaug-Dissert., Leipzig 1882.

and the chloride of which is said to have the composition



Gerdes also examined the nitrate and sulphate of this base.

In the course of further researches<sup>1</sup> Drechsel found that when alkaline solutions were used platinum was present in the electrolyzed fluid. Copper when used as electrode showed a similar behavior; lead was less attacked, gold but very slightly, and palladium not at all.

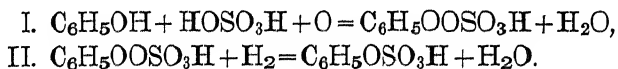
The formation of *phenylsulphuric acid* in living organisms is supposed, like carbamide, to be the result of dehydration. Taking this into consideration, Drechsel carried out the following experiment:

A saturated solution of acid magnesium carbonate was mixed with an equal volume of a solution of magnesium sulphate and the mixture was saturated with commercial carbolic acid.

When this solution was electrolyzed for thirty hours with alternating currents, using platinum electrodes, then the following products were obtained:

- |                          |                                      |
|--------------------------|--------------------------------------|
| 1. $\gamma$ -Diphenol.   | 7. Succinic acid.                    |
| 2. Pyrocatechin.         | 8. Malonic acid (?).                 |
| 3. Hydroquinone.         | 9. n-Valeric acid (?).               |
| 4. Phenylsulphuric acid. | 10. n-Butyric acid (?).              |
| 5. Oxalic acid.          | 11. Some cyclohexanone, <sup>2</sup> |
| 6. Formic acid.          | $\text{C}_6\text{H}_{10}\text{O}$ .  |

According to Drechsel the formation of the phenol ester of sulphuric acid is probably represented by the following equations:



Later Drechsel<sup>2</sup> electrolyzed *normal caproic acid* with alternating currents. The electrolytic solution contained, in a vol-

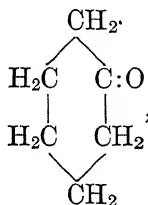
<sup>1</sup> Journ. prakt. Chem. **29**, 229 (1884).

<sup>2</sup> Ibid. **34**, 135 (1886).

ume of 3 liters, 200 g. of caproic acid as magnesium salt and was nearly saturated with acid magnesium carbonate. Platinum electrodes were used. At the end of the experiment the following compounds could be identified in the solution:

- |                   |                     |
|-------------------|---------------------|
| 1. Valeric acid.  | 5. Adipic acid.     |
| 2. Butyric acid.  | 6. Oxycaproic acid. |
| 3. Oxalic acid.   | 7. Glutaric acid.   |
| 4. Succinic acid. |                     |

In a still later research on the electrolysis of *phenol* with alternating currents Drechsel<sup>1</sup> detected phenylsulphuric acid, dioxybenzenes, a number of acids of the fatty acid series, and in addition to these an oil which he identified as hydrophenoketone,



and whose phenylhydrazine compound he was able to isolate. Drechsel regards hydrophenoketone as the origin of the fatty compounds formed. By the direct addition of water to this compound caproic acid results, and this then breaks up into the acids and other decomposition products mentioned above.

Some of the above acids have been mentioned as decomposition products of phenol in the investigation cited on the electrolysis of phenol.

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<sup>1</sup> Journ. pract. Chem. 38, 65 (1888).

## CHAPTER VI.

### ELECTRIC ENDOSMOSE.

By electric endosmose or cataphoresis is meant the often observed phenomenon of the migration or flow of a fluid, under the influence of potential differences, through the diaphragm separating the cathode and anode chambers. This flow or transportation of fluid always occurs in a certain direction, either to the anode or to the cathode, depending upon the nature of the substances and the diaphragm; it has no connection with the electrical phenomena following Faraday's laws. If the rigid diaphragm is replaced by fine suspensions which act like a movable diaphragm, the fluid remains at rest, but the suspended particles migrate, i.e., are urged in the fluid towards the electrode. This directed movement depends undoubtedly upon a polar charge of the suspended particles contrary to that of the water. Since the organic colloids, like the colloid solutions of albumen, carbohydrates, hæmoglobin, indigo, and of natural dyes, act as an extremely fine suspension, cataphoresis also possesses great importance for organic substances, as to their suspension, coagulation and sedimentation phenomena. The scientific treatment of this field has begun. Bredig<sup>1</sup> mentions that the direction of albumen depends upon the chemical composition of the fluid; for instance, whether the aqueous medium is alkaline or acid.

Electric endosmose is of technical importance for the dehydration of organic, finely suspended substances containing very much water, for example, the drying of peat, according

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<sup>1</sup> Ztschr. f. Elektrochemie 9, 739 (1903).

to the experiments of Schwerin.<sup>1</sup> The peat, at a tension of 4 to 5 volts per centimeter peat layer, migrates to the anode and is deposited on the latter in a firm coat, while at the cathode the water becomes clear. Aqueous dye-pastes behave similarly. The technical purification of albumens by cataphoresis is also said to be feasible.

Another field in which cataphoresis, or the convective conduction as the process is also called, has apparently already become of great importance, is the tanning industry.

If the skin to be tanned is brought between the cathode and anode in a dilute tannic-acid solution, a migration of the colloiddally dissolved tannic acid takes place through the skin from the positive to the negative electrode. By a regular slow change of the current direction the tannic-acid solution can be pressed into the pores of the skin and thus a considerable saving in time is accomplished.<sup>2</sup>

*Note.*—It has been known for a long time that many finely divided bodies suspended in water, as gold, copper, graphite, silica, feldspar, sulphur, lycopodium, etc., as well as minute drops of liquids, such as  $\text{CS}_2$  and oil of turpentine, and bubbles of oxygen, marsh-gas, etc., show cataphoresis phenomena. All these are urged in water towards the positive electrode, but in oil of turpentine the direction is reversed except in the case of particles of sulphur; the direction is also reversed for silica in carbon disulphide. The earlier experiments along these lines on solid particles contained in fluids of high resistance were made by Faraday, Jürgensen, Quincke, etc.—Translator.

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<sup>1</sup> Ztschr. f. Elektrochemie 9, 739 (1903); D. R. P. No. 131932 (1901).

<sup>2</sup> S. Foelsing, Jahrb. d. Elektrochemie 2, 269 (1895).

## PART II.

### *ELECTROTHERMIC PROCESSES AND THE SILENT ELECTRIC DISCHARGE.*

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#### CHAPTER I.

##### THEORETICS AND METHODICS.

###### 1. THEORETICS.

ACCORDING to Ohm's law the strength or intensity of the electric current, i.e. the quantity of electricity which is conducted by an electric conductor or a system of conductors in a given time, is directly proportional to the effective electromotive force, and inversely proportional to the resistance of the current field:

$$i = \frac{e}{w},$$

where  $i$  is the current strength,  $e$  the electromotive force or the tension, and  $w$  the resistance. The work which electrical energy can perform in a current field is expressed by the product of the electromotive force existing in this field and the current strength

$$A = e \cdot i,$$

where  $A$  denotes the work to be done.

Substances are known which interpose a more or less strong resistance to the passage of the current, and such whose resist-

ance is so great that practically no passage of the current takes place. The former are called conductors of electricity; the latter non-conductors or insulators. The conductors themselves are in turn again subdivided into two sharply defined classes; those which conduct the current without being materially changed, i.e. the passage of electricity produces no change in the chemical composition of the substance, and those—presenting a remarkable contrast to the former—in which the passage of electricity results in the chemical decomposition of the substance of the conductor at points where the electric current enters and leaves the body, i.e. changes of the substance occur. To the former class of conductors belong all metals and carbon, the conductors of the first class; to the latter the bases, acids, and salts in solution, particularly aqueous solution, or in a molten, and also, under certain conditions, in a solid,<sup>1</sup> state. They form conductors of the second class, or electrolytes.

Ohm's law is equally applicable to both classes. The work which the current can do, however, depends upon the nature of the conductor. If the circuit is completely metallic and closed, the total electric energy can be converted into heat; but if the circuit contains an electrolyte, a large part of the electric energy is used up in the production of chemical and physical effects which occur when the circuit is closed.

To determine in a simple way the connection of the electric energy with the calorific energy caused by it, an electric circuit can be closed by a metallic wire placed in a calorimeter, and the current measured calorifically by the heat effects produced by the different electromotive forces and intensities. The result of such measurements is the equivalence of the heat occurring in the conductor with the electric energy, hence with the product of electromotive force into the electric quantity

$$Q = kei,$$

where  $Q$  denotes the heat generated in the wire. The factor  $k$  is the electrical equivalent of heat, which permits a numerical

<sup>1</sup> See Nernst, on "solid electrolytes," *Zeit. f. Elektrochemie* 6, 41-43 (1899).

comparison of the two forms of energy. It follows, that

$$0.239 \text{ cal} = 1 \text{ volt} \times 1 \text{ coulomb.}$$

If we introduce from Ohm's law the factor  $iw$  for the electromotive force  $e$ , then

$$Q = k \cdot i^2 w.$$

The amount of heat generated in a given time varies directly as the product of the resistance of the conductor into the square of the current strength. This relation is called *Joule's<sup>1</sup> law*, named after its discoverer. The heat which is thus derived only from the current quantities, but not from chemical changes, is also called *Joule's heat*.

If, besides the metallic connections, an electrolyte is included in the closed circuit, a part of the electric energy is used up in chemical work. The electrical energy is then transformed in various ways,—in all parts of the current field heat is developed proportional to the resistance of each separate part and the square of the current strength, but chemical work and material changes and disarrangements in the electrolyte are also accomplished.

In utilizing the heat produced by the current for reactions of organic bodies, only those systems are taken into account in which the current, by forming a spark discharge or luminous arc, is forced either to pass through gases or vapors with high resistance, or to heat wires or filaments to high temperatures. While the extremely high temperatures, which can be attained by means of the voltaic arc in the electric furnace, have through Moissan's investigations become of great importance for mineral chemistry, it is a peculiarity of organic substances, whose conditions of existence, with few exceptions, are connected with relatively low temperatures, and are mostly quite sensitive, that the methods applicable here must allow a fuller scope in temperature than is accorded by the spark discharge or luminous arc. Ruhmkorff's coils, and less often frictional electric machines,

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<sup>1</sup> Phil. May 19, 260 (1841).



are usually employed for giving sparks. The resistance furnaces, in which a tube of carbon is heated by the current, seem more suited for carrying out pyrogenic reactions of carbon compounds. Both heating methods have already been used. Lepsius<sup>1</sup> has employed the luminous arc for decomposing gases and demonstrating volumetric proportions, also for preparing water gas. Bredig<sup>2</sup> made some qualitative tests on the behavior of separate organic fluids towards the luminous arc, while Hofmann and Buff<sup>3</sup> have also investigated the effect of electrically incandescent platinum and iron wires on some gases and vapors. Legler,<sup>4</sup> in his experiments on the incomplete combustion of ether, also employed electrically heated platinum. Moreover, Haber,<sup>5</sup> by making the heated conductor (of platinum, platinum-iridium, or carbon) tube-shaped and conducting the current of gas through the hollow centre in which was placed a glass or porcelain tube, perfected the principle of resistance ovens for the chemical investigations of gases. But these investigations did not lead to an extensive use of these electrical methods for obtaining pyrogenic reactions with organic bodies. Most of the material of such reactions has so far been collected with the spark discharge between metallic electrodes; of late years numerous experiments on the pyrogenic reactions of organic bodies have been undertaken with electrically incandescent wires or filaments.

## 2. THE REACTION TEMPERATURES.

Before taking up the subject of the individual results, some remarks on the attainable temperatures, the possibility of their variation, their measurement and calculation will be made.

No very accurate measurements of the temperatures occurring in the spark discharged are available, great difficulties

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<sup>1</sup> Ber. d. deutsch. chem. Gesellsch. **23**, 1418, 1637, 1642 (1890).

<sup>2</sup> Ztschr. f. Elektrochemie **4**, 514 (1898).

<sup>3</sup> Lieb. Ann. **113**, 129 (1860).

<sup>4</sup> Ibid. **217**, 381 (1883); Ber. d. deutsch. chem. Gesellsch. **18**, 3350 (1885).

<sup>5</sup> Experimental Investigations on the Decomposition and Combustion of Hydrocarbons (Munich, 1896) 43.

being encountered in their determination. Calorific methods are best suited for investigating the temperature of the luminous arc, or the radiant energy is employed for learning the temperature. In the latter case a bolometer or photometer is used.

According to Violle,<sup>1</sup> the temperature of the positive carbon point and of the carbon particles in the voltaic arc equals the evaporation temperature of carbon. This was determined by breaking off the incandescent tip of the carbon and dropping it into a calorimeter. One gram carbon requires 1600 cal. to heat it from 0° up to its evaporation temperature. As 300 cal. are necessary to heat it from 0° to 1000°, 1300 cal. remain for raising the temperature from 1000° to  $x^\circ$ , if  $x$  is the evaporation temperature of carbon. If we take the specific heat of carbon at 0.52, then 1300 cal. represent 2500° more, so that the evaporation temperature of carbon,  $x$ , and the hottest parts of the luminous arc, equal 3500°.<sup>2</sup>

Langley, Paschen, Violle, and Le Chatelier<sup>2</sup> sought to determine the temperature of the heated body by means of the radiant intensity.

The use of the thermopile in the form of Le Chatelier's<sup>3</sup> platinum, platinum-rhodium thermocouple, a so-called pyrometer, has obtained especial importance. This can be used to measure temperatures up to 1700°.<sup>4</sup> The electromotive force is measured either by one of the well-known methods, or else direct reading precision-voltmeters (or galvanometers), whose scales are divided both into millivolts and into the corresponding degrees Celsius or Fahrenheit, are employed. The determination of the

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<sup>1</sup> Compt. rend. **115**, 1273 (1892); **119**, 949 (1894).

<sup>2</sup> Barus, *Die physik. Behandlung und die Messung hoher Temperaturen*, Leipzig, 1892; also Bredig, *Über die Chemie der extremen Temperaturen*, Leipzig, 1901.

<sup>3</sup> Le Chatelier et Boudouard, *Mesure des températures élevées*, Paris, 1900. Le Chatelier, Compt. rend. **114**, 470 (1892) etc. Holborn u. Wien. Ann. **56**, 360 (1895); **59**, 213 (1896); Holborn u. Day, Wied. Ann. **68**, 820 (1899), etc.

<sup>4</sup> Wanner's Optical Pyrometer indicates up to 4000° C. See Journ. Am. Chem. Soc., 1904.

temperature from the electromotive force is based upon the fact that on heating the joint where the platinum wire is fused to the platinum-rhodium wire, an electromotive force of about one millivolt for every 100° C. is produced. The ratio of the electromotive force to the temperature of the fused joint is accurately determined by the Physik-tech. Reichsanstalt, and the result accompanies the calibrated pyrometer. The data always refer to an arrangement whereby the connections between the thermocouple and the conducting wires are at 0°, while the fused joint of the couple is placed in the space whose temperature is to be measured.

The resistance thermometer<sup>1</sup> is extremely convenient for measuring wide ranges of temperature. The electric resistance of pure metals increases with the temperature about 0.4% per degree (C.); but the temperature coefficient for different metals and also for different temperature intervals is by no means constant.<sup>2</sup> If the temperature coefficient is known, for accurate purposes the resistance during the experiment can be measured with a Wheatstone bridge; for less accurate measurements it will often be sufficient to determine the tension of the incandescent wire and the intensity in the current circuit, and to calculate the resistance according to Ohm's law. Care must, however, be taken that the conducting wires connected with the wire whose temperature is being investigated are practically without resistance. For showing the dependence of the resistance upon the temperature an equation of the following form usually suffices:

$$w = a + bt + ct^2,$$

or

$$t = \alpha + \beta w + \gamma w^2.$$

The values  $a$ ,  $b$ , and  $c$ , or  $\alpha$ ,  $\beta$ , and  $\gamma$  are given in the tables. Pyrogenic reactions, whose course remains the same within

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<sup>1</sup> Holborn and Wien, *Wied. Ann.* 56, 383 (1895); 59, 213 (1896). *Calender*, *Phil. Mag.* 32, 104 (1891).

<sup>2</sup> Landolt-Börnstein, *Physik.-Chemische Tabellen*.

larger temperature intervals, permit of a further simplification, naturally at the cost of accuracy. If we make

$$w_t = w_o(1 + \alpha t),$$

in which the range of the respective temperature must be considered in the choice of  $\alpha$ , then

$$t = \frac{w_t - w_o}{\alpha \cdot w_o}.$$

$\alpha$  is for iron about 0.0045, for nickel 0.0036, for platinum 0.0033, and for platinum-iridium (20% iridium) 0.00105, all metals in wire shape. This approximate determination is convenient, even if pyrogenic reactions are brought about by the wire itself, whereby an accurate determination of reaction temperature often becomes illusory for the most various reasons.<sup>1</sup>

### 3. ARRANGEMENTS.

Little can be said about the arrangements to be chosen for the pyrogenic reactions of organic bodies. Both the spark discharge and the luminous arc can be produced in fluids or molten substances. Löb,<sup>2</sup> in decompositions with the luminous arc, employed a small flask with three tubulures, about the shape and size of the boiling-vessel employed in Beckmann's method for determining molecular weights. Each of the two side tubes of equal dimensions supports a thin carbon rod passed through the perforation of a tightly fitting stopper, so that the electrodes in the inside of the vessel are at an angle to one another. The centre tubulure supports a return condenser to which is attached an arrangement for collecting the generated gases. By regulating the volume of the liquid in the decomposition flask the luminous arc can at will be produced in the liquid or its vapor. In the latter case the substance is heated to boiling and the circuit closed as soon as the air in the apparatus is displaced by the vapor.

<sup>1</sup> Löb, *Ztschr. f. Elektrochemie* 7, 903 (1901).

<sup>2</sup> *Ber. d. deutsch. chem. Gesellsch.* 34, 915 (1901).

The degree of decomposition by the voltaic arc depends of course, to a great extent upon the chemical nature of the liquids and vapors in which the luminous arc is produced. While ether, methyl alcohol, ethyl alcohol, glacial acetic acid, and other aliphatic fluids and their vapors are subject to decompositions with very trifling charring, and give products which are chemically closely related to the products started with, benzene, toluene, nitrobenzene, aniline, naphthalene, phenol, and other members of the aromatic series are destroyed, and considerable charring results.

For this reason the method worked out and employed by Löb,<sup>1</sup> replacing the luminous arc by metallic and carbon re-

sistances, proves in general to be more suitable for the purpose of obtaining pyrogenic reactions of organic substances.

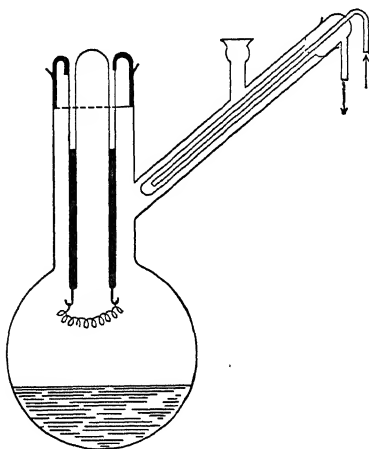


FIG. 8.—Electropyrogenizer.

A round flask with a long neck is closed with a thrice-perforated stopper. Two small glass tubes with strong platinum hooks sealed in the lower ends are passed through the two side perforations; a little mercury forms the connection between the hooks and the conducting wires leading in. Or, strong wires bent into hooks at one end are directly stuck through the stopper, which can be done with-

out injuring the tight fit. The incandescent wire, a metallic wire of about 0.2 mm. diameter, is fastened to the hooks by wrapping it around or hooking it on. A return condenser is placed in the centre perforation. Löb, when making decompositions in a perfectly air-tight apparatus and under diminished pressure, replaces the stopper by a ground-glass stopper in which the

<sup>1</sup> Löb, *Ztschr. f. Elektrochemie* 7, 904 (1901); 10, 505 (1904).

small tubes with platinum hooks are sealed in. The return condenser, which serves as an internal cooling apparatus, is attached to the side; another glass tube sealed in the wall of the flask (not shown in the figure) serves for admitting air, or for the passage of other gases for special purposes (see Fig. 8). This apparatus is particularly adapted for pyrogenic reactions of high-boiling substances in a partial vacuum. The substance is placed in the round bulb. Direct heating converts it into vapor, which, after the air has been removed, is permanently in contact with the incandescent wire.

## CHAPTER II.

### THE SPARK DISCHARGE AND THE VOLTAIC ARC.

#### 1. THE SPARK DISCHARGE.

It is well known that most of the gaseous hydrocarbons of the aliphatic series when exploded with an excess of oxygen are converted into the end-products of combustion, carbonic acid and water. This fact is made use of in quantitative gas analysis. The combustion is often not complete; intermediate products can be obtained if we start with hydrocarbon derivatives instead of the hydrocarbons themselves.

Berthelot gave a comprehensive exposition of the results known at that time on the effect of the spark discharge upon the formation and decomposition of carbonic acid and hydrocarbons and the herewith occurring equilibrium phenomena (Berthelot, *Essai de Mécanique Chimique* II, 336-362, Paris, 1879).

**Methane.**—The induction sparks decompose this substance into carbon and hydrogen (Hofmann<sup>1</sup> and Buff), which fact Dalton had already observed.

Berthelot<sup>2</sup> obtained hydrogen, carbon and acetylene. If the latter is continually gotten rid of, the greater part of methane can be converted into acetylene, otherwise the latter is decomposed and changed in a complex manner.

Methane is also produced by the reaction of carbon monoxide with hydrogen under the influence of the induction spark

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<sup>1</sup> Lieb. Ann. **113**, 129 (1860).

<sup>2</sup> Ibid. **123**, 211 (1862).

(Brodie <sup>1</sup>), a fact which explains the formation of hydrocyanic acid from carbon monoxide, hydrogen, and nitrogen, as will be mentioned further on.

**Ethylene** is decomposed by the spark discharge into its elements (Dalton, Hofmann, and Buff <sup>2</sup>). According to Wilde,<sup>3</sup> acetylene is first formed, and is then decomposed into its elements. Besides, according to Thénard and Berthelot,<sup>4</sup> a fluid and solid product are produced.

W. G. Mixer <sup>5</sup> has recently investigated the combustion phenomena of several hydrocarbons by means of a weak electric spark discharge, and has proven among other things that ethylene can also yield acetic acid besides carbonic acid. The pressure under which the gases react is important for the course of the experiment. Mixer sought to determine the relative reaction velocities as compared with that of an oxyhydrogen mixture, under equal conditions.

**Acrolein**,  $\text{CH}_2\text{:CH}\cdot\text{CHO}$ , according to E. von Meyer,<sup>6</sup> is formed when ethylene with an excess of oxygen is exploded in a eudiometer.

**Formic Acid**.—Wilde <sup>7</sup> found that the action of the electric spark on gaseous mixtures of oxygen and alcohol, hydrogen and carbon dioxide, and methane and carbon dioxide, produced formic acid. In the first and last mentioned of these mixtures *acetic acid* is also formed.

**Acetylene**.—The spark acts, as already mentioned, by reason of its high temperature which, according to Berthelot,<sup>8</sup> is sufficient to produce acetylene from a mixture of carbon disulphide and hydrogen, sulphur being precipitated.

<sup>1</sup> Lieb. Ann. 169, 270 (1873).

<sup>2</sup> Ibid. 113, 129 (1860).

<sup>3</sup> Ztschr. f. Chemie 2, 735 (1866).

<sup>4</sup> Traité de Mécanique chimique II, 350 (1879).

<sup>5</sup> Ann. Journ. of Sc. [4] 4, 51 (1897); Journ. Chem. Soc. 73, 246 (1898); Proceed. Chem. Soc. 39 (1898).

<sup>6</sup> Journ. f. prakt. Chemie [2] 10, 113 (1874).

<sup>7</sup> Bull. soc. chim. [2] 5, 267 (1866).

<sup>8</sup> Tommasi Traité d'Electrochimie 715 (1879).



**Hydrocyanic Acid.**—Berthelot<sup>1</sup> obtained this substance by passing the electric spark through a mixture of acetylene and nitrogen. The acid is in fact frequently produced in far-reaching decompositions by the electric spark; thus from a mixture of ethylene or aniline vapor with nitrogen (Berthelot<sup>1</sup>), from a mixture of acetylene with nitric oxide (Huntington<sup>2</sup>), ammonia with benzene, or ether and nitrogen (Perkin<sup>3</sup>), etc. The reactions are also in a certain sense reversible. Hydrocyanic acid is readily split up by the current (Gay-Lussac<sup>4</sup>), and in the presence of hydrogen (Berthelot<sup>5</sup>), into acetylene and nitrogen.

The union of acetylene and nitrogen to hydrocyanic acid takes place rather smoothly if the easy decomposability of acetylene is lessened by dilution with hydrogen, as was already done by Berthelot.<sup>6</sup> His experiments were recently again taken up by Gruszkiewicz.<sup>7</sup> The electrodes were blackened by a deposition of carbon except with a maximum content of acetylene of 5 per cent. by volume (composition of the gas mixture: 5 per cent. acetylene, 5 per cent. nitrogen and 90 per cent. hydrogen).

Gruszkiewicz obtained better results by using a mixture of carbon monoxide, hydrogen, and nitrogen. He found that the proportion of the components was essentially decisive for the yield and the reaction velocity. A mixture approximately corresponding in composition to that of water gas, Dowson gas, generator gas, etc., gave encouraging results. Thus, if 3 liters of a gas mixture of 54.62 per cent. CO, 24.88 per cent. N<sub>2</sub>, and 20.50 per cent. H<sub>2</sub> were permitted to flow for an hour through the space through which the sparks were discharged, then about 12 cc. hydrocyanic acid were obtained. Carbon dioxide, like carbon monoxide, is reduced by hydrogen in the spark dis-

<sup>1</sup> Bull. soc. chim. [2] 13, 107 (1869).

<sup>2</sup> D. R. P. No. 93852 (1895).

<sup>3</sup> Jahresb. f. Chemie. 399 (1870).

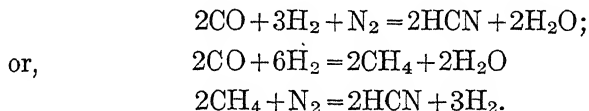
<sup>4</sup> Ann. chim. phys. 78, 245 (1811); Gilberts Ann. 1811.

<sup>5</sup> Bull. soc. chim. [2] 13, 107 (1869).

<sup>6</sup> Traité de Mécanique chimique II, 355 (1879).

<sup>7</sup> Ztschr. f. Elektrochemie 9, 83 (1903).

charge, and changed, by uniting with nitrogen, into hydrocyanic acid. The reaction can be shown in the equation,



Cyanogen shows the same easy decomposability as hydrocyanic acid. Both Berthelot<sup>1</sup> and Hofmann and Buff<sup>2</sup> observed that cyanogen was decomposed into its elements by the action of the electric spark. The least trace of water in the gas caused the formation of hydrocyanic acid and acetylene.

The observation of Morrens,<sup>3</sup> who claimed to have obtained cyanogen in an atmosphere of nitrogen by passing the induction spark between two carbon electrodes, is therefore incorrect. The decomposition of cyanogen by the action of the electric spark has, moreover, been noted by Davy, and by Andrews and Tait.<sup>4</sup>

**Ethyl Alcohol.**—In an atmosphere of ethyl-alcohol vapors, M. Quet<sup>5</sup> and Perrot<sup>6</sup> obtained, besides some carbon, a substance which exploded on being heated, the chemical nature of which they were unable to determine. The liquid became acid but Perrot found that no water was formed in the decomposition of the alcohol; he was also unable to prove the presence of carbonic acid gas. Melly<sup>7</sup> and Lommel<sup>8</sup> made similar experiments, the latter employed a Holtz machine. The gas escaping in the decomposition of the alcohol probably contains acetylene and ethylene.

**Ethyl Ether.**—According to Wilde's<sup>9</sup> experiments, ethyl ether, under reduced pressure, also yields ethylene besides other

<sup>1</sup> Compt. rend. 82, 1360 (1876).

<sup>2</sup> Lieb. Ann. 113, 129 (1860).

<sup>3</sup> Compt. rend. 48, 342 (1859).

<sup>4</sup> Journ. Chem. Soc. 13, 344 (1861).

<sup>5</sup> Compt. rend. 46, 903 (1858).

<sup>6</sup> Ibid. 46, 180 (1858); 47, 351 (1859).

<sup>7</sup> Tommasi, Traité d'Electrochimie, 724 (1879).

<sup>8</sup> Ibid., 725 (1879).

<sup>9</sup> Ztschr. f. Chemie 2, 735 (1866).

gases, and a deposition of carbon. Truchot<sup>1</sup> observed methane and hydrogen besides the ethylene. Perrot,<sup>2</sup> by the action of bromine upon the gases obtained by the action of the electric spark, was able to isolate a liquid,  $C_3H_5Br_3$ , boiling at  $135^{\circ}$ – $140^{\circ}$ , and isomeric with tribromhydrin. Klobukow,<sup>3</sup> by heating ether vapor to  $250^{\circ}$ – $300^{\circ}$  and passing the spark through the latter, obtained carbon monoxide, hydrogen, methane, ethylene, and acetylene.

**Acetone.**—Wilde<sup>4</sup> investigated the action of the electric spark on acetone vapor in a Torricelli vacuum. Acetylene was formed in the gas mixture and carbon was deposited on the sides of the vessel.

**Formic Acid**, on the contrary, does not yield acetylene (Wilde). Nor could he prove the presence of this gas in the decomposition of *acetic acid*.

**Methylamine.**—The electric spark, when passed through methylamine vapor by Hofmann and Buff,<sup>5</sup> gave primarily hydrogen and methylamine hydrocyanide; further action brought about complete decomposition, tarry substances being deposited.

**Trimethylamine** was investigated by the same authors. It also is completely broken up, tarry products being formed.

**Ethylamine.**—Hofmann and Buff obtained tar-like products and a non-alkaline gas having an odor like that of ethyl cyanide.

The experiments carried out on the behavior of compounds of the aromatic series when subjected to the electric spark have so far given very few results.

**Benzene.**—Destrem<sup>6</sup> investigated the action of the induction spark between two platinum points on benzene, and obtained a gas mixture of acetylene and hydrogen, while the liquid contained diphenyl and a crystalline substance which was not closely investigated. Benzene vapor, under reduced pressure,

<sup>1</sup> Compt. rend. **84**, 714 (1877).

<sup>2</sup> Ibid. **46**, 180 (1858).

<sup>3</sup> Journ. f. prakt. chemie [2] **34**, 126 (1886).

<sup>4</sup> Bull. soc. chim. [2] **5**, 267 (1866).

<sup>5</sup> Lieb. Ann. **113**, 129 (1860).

<sup>6</sup> Bull. soc. chim. **42**, 267 (1884).

is decomposed by the electric spark, likewise producing acetylene (Wilde<sup>2</sup>).

**Toluene.**—Destrem<sup>1</sup> obtained from toluene, as from benzene, acetylene, and hydrogen. The liquid contained, besides diphenyl, a solid substance which was not further investigated.

**Naphthalene.**—Wilde<sup>2</sup> also investigated the behavior of naphthalene vapor under reduced pressure when subjected to the action of the induction spark. He obtained a gas mixture containing acetylene.

**Aniline.**—Destrem<sup>3</sup> investigated the action of the electric spark from an induction apparatus on aniline vapor, and observed a decomposition into acetylene, hydrogen, hydrocyanic acid, and nitrogen.

Pyrogenic reactions of organic compounds with the "electric flame," (flaming discharge) as produced at a lower tension and higher intensity than required for the production of the spark (at about 2000–4000 volts and 0.05–0.15 amp.) have not yet been carried out.

According to the investigations of W. Muthmann and H. Hofer,<sup>4</sup> interesting results are also to be expected in its application to organic compounds.

## 2. THE VOLTAIC ARC.

As already mentioned in the introduction, the enormously high temperature of the luminous arc is only applicable in certain cases to organic compounds.

Several reactions have, however, become of fundamental, theoretical and practical importance; for instance, Berthelot's acetylene synthesis, the preparation of carbides, and some other processes.

<sup>1</sup> Bull. soc. chim. **42**, 267 (1884).

<sup>2</sup> Ibid. **5**, 267 (1866).

<sup>3</sup> l. c., see also Jahresb. f. Chem. **272** (1884).

<sup>4</sup> Ber. d. deutsch. chem. Gesellsch. **36**, 438 (1903).

**Acetylene.**—Berthelot<sup>1</sup> showed that carbon and hydrogen combined to acetylene on passing the voltaic arc over carbon points in an atmosphere of hydrogen. The synthesis of acetylene from its elements first made possible the complete synthesis of a whole series of organic compounds. Acetylene, as is well known, is produced by the decomposition of many organic compounds at high temperatures. Bredig<sup>2</sup> thus obtained acetylene, besides other hydrocarbons, when he produced the luminous arc in liquid petroleum.

**The Metal Carbides.**—These are of great technical and scientific importance. They have been repeatedly and thoroughly described, hence a reference to various works upon this subject will suffice here.<sup>3</sup>

Bolton<sup>4</sup> succeeded in combining *chlorine and carbon*. He employed the voltaic arc between carbon electrodes in an atmosphere of chlorine. Perchloroethane is principally produced; hexachlorobenzene is formed in lesser quantity. As both of these chlor-hydrocarbons are produced by the complete chlorination of carbon tetrachloride, Bolton assumes their intermediate existence; the intermediate occurrence of gaseous or fluid compounds like perchlorethylene does not seem improbable. Bromine and iodine appear to react analogously (Bolton<sup>4</sup>); experiments with the latter halogens yet await a scientific treatment. They would undoubtedly prove remunerative.

Löb<sup>5</sup> has made several other decompositions by means of the voltaic arc between carbon points. These were carried out with the following vapors and liquids:

**Methyl Alcohol** yields formic acid, and also about 39 per cent. methane, 45 per cent. hydrogen, small quantities of carbonic

<sup>1</sup> Ann. chim. phys. [4] 13, 143 (1868); see also Berthelot: Essai de Mécanique Chimique II, 332-336 (1879).

<sup>2</sup> Ztschr. f. Elektrochemie 4, 514 (1898).

<sup>3</sup> Moissan, The Electric Furnace, Ahrens: Die Metallkarbide (Sammlung chemisch-technischer Vorträge), Stuttgart, 1896, Haber: Grundriss der technischen Elektrochemie, München und Leipzig, 1898. See also, "Recent literature on carbides," Journ. Am. Chem. Soc. 1904, p. 200.—Trans.

<sup>4</sup> Ztschr. f. Elektrochemie 8, 165 (1902); 9, 209 (1903).

<sup>5</sup> Ber. d. deutsch. chem. Gesellsch. 34, 915 (1901).

acid, carbon monoxide, and acetylene. Formaldehyde is not formed.

**Glacial Acetic Acid** yields about 35 per cent. carbon monoxide, 26 per cent. hydrogen, 15.5 per cent. carbonic acid, and 12 per cent. saturated and 7 per cent. unsaturated hydrocarbons.

**Benzene.**—The benzene is colored brown and is considerably charred; no substance could be isolated from the liquid. The escaping gas consists of 86–90 per cent. hydrogen as well as small quantities of saturated and unsaturated hydrocarbons.

**Naphthalene** likewise yields chiefly hydrogen, the residue being greatly charred.

**Cyanogen** is completely decomposed by the voltaic arc, as shown by Hofmann and Buff.<sup>1</sup>

**Cyanides.**—The attempts to prepare cyanides by the direct or indirect union of nitrogen and carbon must be mentioned here; they are of importance particularly for the problem of utilizing atmospheric nitrogen. Since the reactions take place at a high temperature, we can also make use of electrically produced heat, as suggested by Readmann;<sup>2</sup> but in his process—a mixture of oxides or carbonates of alkalies, or earthy alkalies, with carbon is heated in the voltaic arc between two carbon points in the presence of nitrogen—electrolysis occurs as an important factor. The conditions are similar in his attempts, undertaken with Gilmour,<sup>3</sup> to prepare potassium ferrocyanide.

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<sup>1</sup> Lieb. Ann. **113**, 129 (1860).

<sup>2</sup> Eng. Pat. No. 6621 (1894).

<sup>3</sup> Eng. Pat. No. 24116 (1892).

### CHAPTER III.

#### THE UTILIZATION OF CURRENT HEAT IN SOLID CONDUCTORS.

**Methane.**—Davy decomposed methane with an electrically incandescent platinum wire into carbon and hydrogen, an effect which was also later obtained by Hofmann and Buff<sup>1</sup> with an electrically incandescent iron spiral.

**Ethylene**, according to the last named investigators,<sup>1</sup> likewise breaks down, under similar conditions, into its elements.

**Cyanogen.**—Cyanogen also is completely split up by an incandescent iron wire into carbon and nitrogen.

Haber<sup>2</sup> has made some experiments regarding the decomposition of several hydrocarbons in the electric furnace. The gas current was conducted through a glass or porcelain tube which was placed in an electrically heated tube of platinum, platinum-iridium, or carbon.

**Hexane.**—No considerable decomposition of hexane vapor occurs at about 600°; at 800°–940°, however, there were produced the following percentages of gases, based on 100 per cent. of the vaporized hydrocarbon:

Methane. ....	27.77%
Olefines (ethylene). . . .	22.14%
Acetylene. ....	1.00%
Hydrogen. ....	2.44%
Benzene. ....	6.76–10%
Carbon. ....	3.27%
Tar. ....	29.22%

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<sup>1</sup> Lieb. Ann. 113, 129 (1860).

<sup>2</sup> Experimental-Untersuchungen über Zersetzung und Verbrennung von Kohlenwasserstoffen, 43–77 Munich (1896).

At a still higher temperature hexane is for the greater part converted into its elements.

**Trimethylethylene** is split up at 930°–940° in the following manner. From 100 per cent. of material started with there were obtained.

Methane. ....	27.72%
Ethylene. ....	8.10%
Hydrogen. ....	1.76%
Gaseous by-products. ...	4.46%
Acetylene. ....	0.30%
Carbon. ....	5.09%
Benzene. ....	8.00–13.41%
Tar. ....	33.71–39.12%

The above figures represent percentages by weight. At 1000° trimethylethylene is also extensively decomposed.

**Ethyl Ether.**—For obtaining a slow combustion of the ether, Legler<sup>1</sup> passed a mixture of ether vapor and air over an electrically incandescent platinum wire and obtained a mixture of formic acid, acetic acid, formaldehyde, acetaldehyde, and hexaoxymethylene peroxide  $(\text{CH}_2\text{O})_6\text{O}_3 + 3\text{H}_2\text{O}$ .

Löb has recently carried out a great number of pyrogenic reactions and syntheses, employing the already described arrangement (p. 242) with electrically incandescent metallic wires and carbon filaments.

**Methyl Alcohol.**<sup>2</sup>—On employing a cherry-red incandescent iron wire, this substance yielded, besides formic acid and a little trioxymethylene, a gas mixture containing about 72 per cent. hydrogen, 20 per cent. carbon monoxide, 6.5 per cent. methane, and traces of carbon dioxide. The figures represent percentages by volume, the same as below.

**Chloroform.**<sup>3</sup>—This compound, when brought into contact with an incandescent wire of iron, nickel, platinum, or platinum-iridium heated to 850°–950°, is decomposed, there being formed perchlorbenzene (10%), perchlorethane (12%), and perchlor-

<sup>1</sup> Ber. d. deutsch. chem. Gesellsch. 18, 3350 (1885).

<sup>2</sup> Ibid. 34, 917 (1901).

<sup>3</sup> Ztschr. f. Elektrochemie 7, 903 (1901).

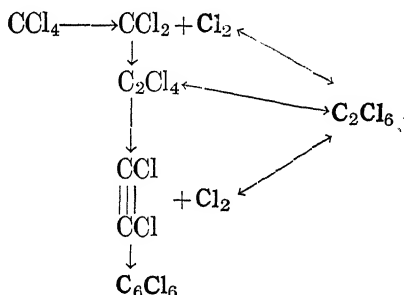




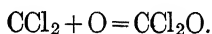
The arrows show the direction and the possible reversibility of the reactions; stable end-products are printed in heavy type.

**Carbon Tetrachloride.**<sup>1</sup> —This compound, when decomposed alone by an arrangement similar to that used for chloroform, gives off great quantities of chlorine; perchlorbenzene, perchlorethane (in very trifling quantity), and perchlorethylene are also produced. The presence of water in this case also increases the yield of carbon monoxide. Aniline leads to triphenylguanidine, some resin being also formed.

The scheme of decomposition for tetrachlormethane is the following:



If air is blown simultaneously with the tetrachlormethane vapors against the incandescent wire, there is produced phosgene, which is probably formed by direct oxidation of dichloromethylene:



**Perchlorethylene**<sup>2</sup> yields a gas mixture of chlorine and a little carbon monoxide, and also phosgene in the presence of air. The residue in the flask consists principally of perchlorbenzene besides traces of perchlorethane. Addition of water considerably increases the quantity of carbon monoxide.

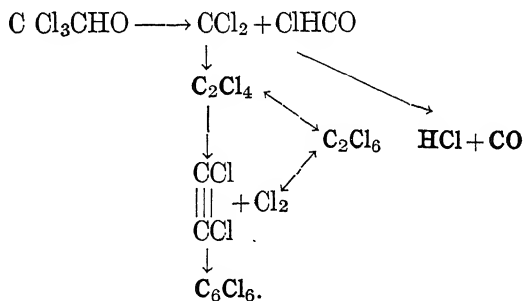
**Chloral Hydrate,**<sup>3</sup> when subjected to pyrogenic decomposi-

<sup>1</sup> l. c.

<sup>2</sup> l. c.

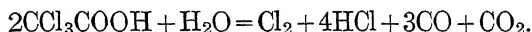
<sup>3</sup> Ztschr. f. Elektrochemie **10**, 504 (1904).

tion alone or mixed with water vapors, breaks up in the same manner. The reactions are expressed in the following scheme:



Besides the products observed in the decomposition of chloroform, carbon monoxide also occurs as a direct decomposition product of the unstable formylchloride.

**Trichloroacetic Acid** is completely decomposed at higher temperatures into gases; Joist<sup>1</sup> could detect hydrochloric acid, chlorine, carbon monoxide, and carbon dioxide, besides traces of phosgene. The decomposition takes place, perhaps with the aid of moisture, as shown in the equation:



Phosgene is formed secondarily from chlorine and carbon monoxide.

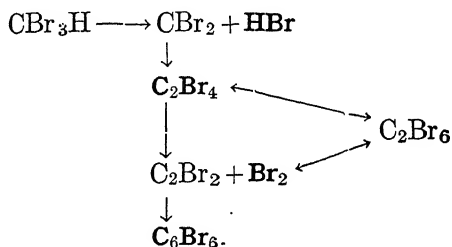
**Acetyl Chloride** breaks up (Joist<sup>1</sup>) completely into approximately equal volumes hydrochloric acid, carbon monoxide, and unsaturated hydrocarbons (mostly ethylene). The reaction is expressed in the equation:



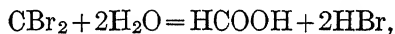
**Bromoform** splits off hydrobromic acid and some free bromine, and yields as chief product perbromethylene, also perbrom benzene (Joist<sup>1</sup>). Hexabromethane occurs only in traces; this was to be expected on account of its easy decomposability into bromine and perbromethylene. Some carbon monoxide

<sup>1</sup> The experiments have not yet been published. Bonn (1904).

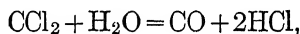
escapes. If the bromoform vapors are mixed with aqueous vapors the products remain the same; but no gas is evolved, and the water contains, besides hydrobromic acid, small quantities of formic acid. The following expresses the decomposition:



Presence of water determines the reaction:



while with chloroform the reaction is



carbon monoxide being produced.

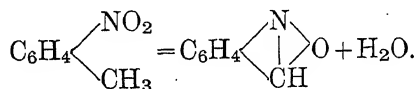
**Benzene**, as is well known, is easily converted at high temperatures into diphenyl and complex hydrocarbons. Löb's<sup>1</sup> method is very well suited for preparing diphenyl on a small scale. Metallic wires serve the same purpose as carbon filaments. Diphenylbenzene occurs as a by-product in small quantity.

**Nitrobenzene**, blown in vapor form against the incandescent wire, decomposes violently, sometimes explosively, producing a charred mass and large quantities of nitric oxide. The reaction is moderated by diluting the vapors with aqueous vapor, but the obtainable products are so complex that their determination has not yet been accomplished (Löb<sup>2</sup>).

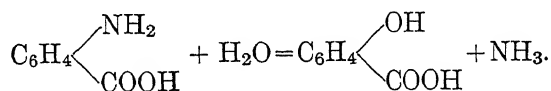
<sup>1</sup> Ztschr. f. Elektrochemie 8, 777 (1902).

<sup>2</sup> Ber. d. deutsch. chem. Gesellsch. 34, 918 (1901); Ztschr. f. Elektrochemie 8, 775 (1902).

**o-Nitrotoluene.**—Although the pure vapors of o-nitrotoluene behave like those of nitrobenzene, o-nitrotoluene diluted with aqueous vapors yields anthranilic acid, in addition to a little o-cresol and salicylic acid and considerable resinous substances (Löb<sup>1</sup>). It is possible that anthranil is primarily formed from o-nitrotoluene, water being split off; the anthranil is then converted into anthranilic acid by the highly heated steam, just as by boiling with alkalies:



The presence of salicylic acid must evidently be referred to the action of the hot aqueous vapors upon anthranilic acid:



Slight traces of ammonia could be detected. The o-cresol was evidently formed from o-nitrotoluene and aqueous vapor, with splitting off of nitrous acid.

The material of the glower is mostly without any influence on the reaction. Platinum, platinum-iridium, nickel, iron and carbon gave qualitatively equal results; only copper wires are not applicable for the preparation of anthranilic acid. They primarily cause a reduction to o-toluidine and then complete combustion is brought about by the copper oxide which is formed.

**Aniline.**<sup>2</sup>—This compound is colored brown, ammonia is split off and some gas evolved. Diphenylamine and carbazole could be isolated.

**Diphenylamine.**<sup>2</sup>—On conducting the vapors of this substance mixed with those of chloroform over metallic glowers,

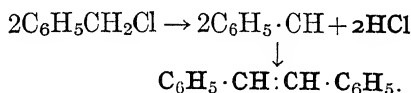
<sup>1</sup> Ztschr. f. Elektrochemie 8, 776 (1902).

<sup>2</sup> Ber. d. deutsch. chem. Gesellsch. 34, 918 (1901); Ztschr. f. Elektrochemie 7, 913 (1901).

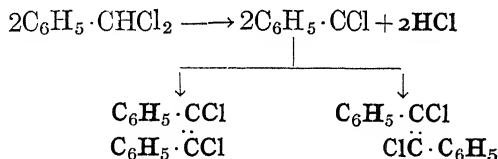
diphenylamine combines with chloroform and gives a small yield of acridine.

**Benzyl Chloride**, *benzal chloride* and *benzotrichloride*, when subjected like chloroform to pyrogenic decomposition, behave quite like the latter compound; a dissociation into hydrochloric acid, or chlorine and phenylmethylene, or chlorophenylmethylene, seems to occur first (Löb<sup>1</sup>).

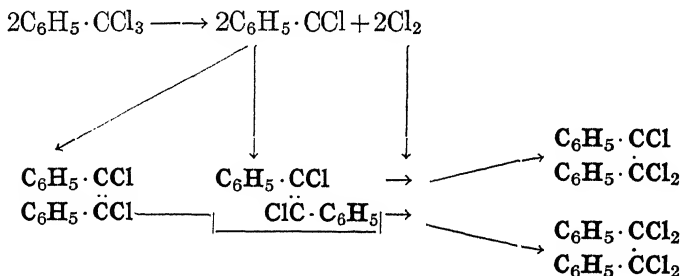
**Benzal Chloride** gives smoothly stilbene, with splitting off of hydrochloric acid:



Benzal chloride also splits off hydrochloric acid, but no chlorine; a mixture of  $\alpha$ - and  $\beta$ -tolane dichlorides results:



**Benzotrichloride** at first gives off chlorine, which does not, however, escape, but is absorbed by a part of the primarily formed tolane-dichlorides; these are thereby converted into tolanetrichloride and tetrachloride.



<sup>1</sup> Ber. d. deutsch. chem. Gesellsch. **36**, 3059 (1903); Ztschr. f. Elektrochemie **9**, 903 (1903).

If a mixture of benzotrichloride and water is subjected to pyrogenic decomposition, the yield of toluene dichlorides, tri- and tetrachlorides is very small, although these substances do not entirely disappear. Benzaldehyde and benzoic acid become the chief products. The benzaldehyde is apparently the reaction product of chlorophenylmethane with water, and the benzoic acid the oxidation product of the benzaldehyde by the intermediately occurring chlorine. Benzalchloride, in the presence of water, gives benzaldehyde; no benzoic acid is formed.

## CHAPTER IV.

### THE SILENT ELECTRIC DISCHARGE AND THE ACTION OF TESLA-CURRENTS.

#### I. THE SILENT ELECTRIC DISCHARGE.

WHILE the action of the induction spark upon organic bodies, gases and vapors is undoubtedly a thermic process, in the silent electric discharge the electric energy plays a more important part, either as such or in the form of radiant energy. In this case we are dealing with a constant passage of an electric current through gases. Even if the theory of the conduction in gases is still in its primitive stages, many phenomena already point to ionic formations or electron effects. The silent electric discharge takes place continuously between two conductors separated by a dielectric such as glass, or gases, if the potential difference of the two conductors exceeds a certain value.

In rarefied gases the discharge is accompanied by luminous appearances (glow discharges), which are often suited for investigations in spectrum analysis; under ordinary pressure and in daylight the gases do not glow; but in the dark and with a sufficiently high tension, even without rarefaction, the glow occurs.

The rise in temperature during the discharge is trifling; therefore reactions which are brought about by the latter's influence often assume a different rôle than those produced by the induction spark. In the latter case stable compounds are produced, which is very natural, considering the high temperature. The formation of labile, often endothermic substances, is incited by the silent electric discharge. These substances are easily decomposed by stronger calefaction. The great value of these reactions for simple syntheses—as employed by nature in plants



for producing the labile compounds, which serve as plant nourishment, from the most stable products started with—lies in this property. This problem is extremely important. The synthesis of substances important for nature—the carbohydrates, albumens—in the laboratory with our usual chemical resources is only a first step in the realm of actual synthesis. This will only be found when we can follow the paths which nature herself chooses in preparing her products. Her methods are undoubtedly much simpler than the artificial, chemical processes that we must make use of in reaching the same goal. The whole primary material upon which we can base the formation of the most various substances of organic nature is the atmosphere—are carbonic acid, oxygen, nitrogen, and water. The synthesis of complex substances from these materials is known to take place under the influence of light rays and the absorption of energy. Such a transformation of a system of lower energy into one of higher energy usually occurs only at high temperatures. The silent electric discharge occupies a prominent place among the forms of energy which, like light, favor endothermic reactions at ordinary temperatures.

Berthelot,<sup>1</sup> in pointing to the nature of the reactions occurring under its influence, which are particularly similar to those of plants, advanced the following views: In clear weather there exists between two strata of air only one metre apart a potential difference of 20–30 volts which, in rainy weather, can increase to about 500 volts. Reactions can already take place under the influence of such tensions; thus at 7 volts a fixation of nitrogen by carbohydrates can already occur; the decomposition of carbonic acid requires higher tensions.

Opportunities for reactions on the surfaces of plants, by the formation of potential differences, are likewise continually present. In other words, Berthelot ascribes a leading part in natural syntheses to atmospheric tensions, which can neutralize one another in the form of invisible discharges (convective discharges) through thin strata of air acting like dielectrics.

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<sup>1</sup> Compt. rend. **131**, 772 (1900).

Even if this hypothesis does not seem to be scientifically well founded, it is nevertheless suitable for showing the importance of this but little investigated domain.

We still know nothing of the consumption of energy in the reactions produced by the silent electric discharge. The spent energy can be easily determined by employing certain current conditions; it is difficult to calculate experimentally the utilized energy; this is due to the insignificance of the obtained reactions and the simultaneously occurring heat quantities.

The fact that Faraday's law is not applicable shows that the reactions which are caused by the discharge are not of a purely electrochemical nature. The chemical effect is usually larger than can be accounted for by the minimum quantities of electricity. As shown by the kind of reactions, thermic effects are also unlikely, although an influence of the temperature produced by the discharge is always manifest. The supposition is more probable that the invisible electric discharge, in which cathode and ultra-violet rays are present, introduces into the system great quantities of kinetic energy by the movement of electrons; this energy is then transformed into chemical energy. This kinetic energy would then have to be equivalent to the heat of formation of the occurring substances, taking into account the part directly converted into heat. Bichat and Guntz<sup>1</sup> have shown by a simple example, that of ozone, that the heat developed in the induction tube and calorimetrically measured, plus the heat of formation of the produced ozone, is equal to the calorific equivalent of the spent electrical energy.

The actual efficiency of ozonizers is extremely small. With the best ozone apparatus and under the most favorable circumstances only about 15 per cent. of the total energy can be utilized for the chemical reaction.

#### a. Arrangements.

The well known and variously shaped small ozonizers of Berthelot and Siemens are generally satisfactory for scientific

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<sup>1</sup> Ann. chim. phys. [6] 19, 131 (1890).

experiments. According to a recommendation of Losanitsch and Jovitschitsch the apparatus are suitably called "electrizers."

The principle employed in their construction is always the same. An air space or chamber, chosen as narrow as possible, exists between two conductors, either metals or electrolytes, which are connected with the terminals of an induction coil.

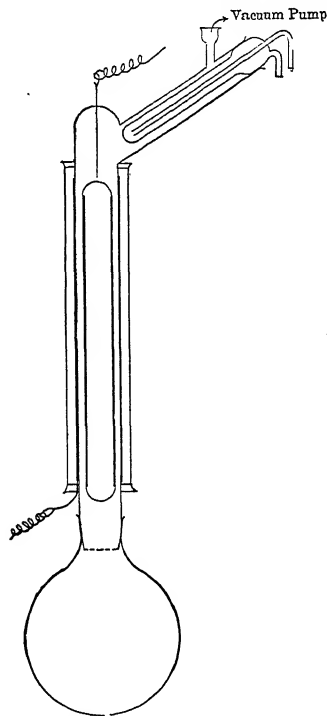


FIG. 9.

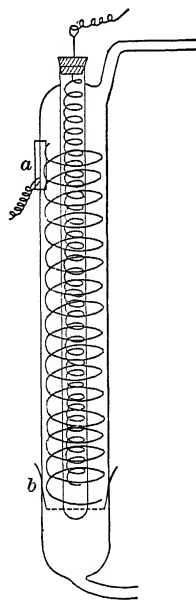


FIG. 10.

The metals serving as electrodes are in most cases separated—electrolytes of course always—from the discharging chamber by thin glass walls. Suitable small tubes attached to the apparatus afford means of ingress and egress for the gases or vapors to be acted upon. The space between the walls in the discharging chamber is of great influence (A. de Hemptinne <sup>1</sup>).

Some apparatus used by myself in experiments as yet unfinished may be mentioned here. The difference from former

<sup>1</sup> Bull. de l'Acad. roy. de Belg. [3] 34, 269 (1897).

constructions exists (in Fig. 9) in the constant production of the vapors in a flask with a ground-glass neck made to fit one end of the induction tube; the flask contains the reaction fluid. This apparatus has an arrangement for cooling the vapors and one for working under diminished pressure. In Fig. 10 the apparatus can be taken apart at the ground-glass connection *b* in such a way that liquids, solids, and electrodes of various materials, especially for investigating catalytic effects, can be brought into it. The current connections with the outer coat is made in Fig. 10 by means of a platinum loop *a*, fused into the side of the tube, in which is hooked the spiral electrode of any kind of metal wire.

Special attention in these experiments must be paid to the interrupter (rheotome<sup>1</sup>); platinum, and mercury circuit-breakers and electrolytic ones are applicable. The former possesses the disadvantage of great wear and tear, and in prolonged experiments requires frequent regulation. If kept clean, the mercury circuit-breaker is very convenient. The Wehnelt circuit-breaker interrupts high current strengths very exactly, and, when suitably made, can be used both with alternating and direct currents. To save the consumption of platinum I construct the electrolytic interrupters by placing in front of a large carbon plate the point of a nickel wire 2 mm. thick as active electrode in a 2-3% sodium-hydroxide solution. Glass worms regulate the temperature with high current strengths. This simple and cheap arrangement has proven serviceable.

### b. Chemical Results.

The action of the silent electric discharge upon organic compounds takes its starting point in the observation that oxygen under its influence is polymerized to ozone. Although the work done in this field, which until recently was chiefly carried on by the French school, has not yet shown great practical results, we need not doubt that these phenomena deserve

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<sup>1</sup> See also Leitfaden des Röntgenverfahrens, published by Dessauer and Wiesner, Berlin, 1903.

the greatest interest and are closely related, as already emphasized, to the fundamental questions of synthesis in general. Besides the experiments on the behavior of organic vapors, the observations which have been made on the synthesis of simple organic compounds from carbonic acid and carbon monoxide—substances which we are not accustomed to regard as organic—are of particular interest. The results so far obtained are mentioned below. We are mostly indebted to Berthelot's investigations along this line of work.

### *I. Carbonic Acid and Carbon Monoxide.*

**Carbonic Acid.**—Berthelot<sup>1</sup> observed the decomposition into carbon monoxide and oxygen. The reaction is reversible, an equilibrium occurs, in which, however, the partially ozonized oxygen converts carbon monoxide into carbonic acid and a solid carbon suboxide,  $C_4O_3$ , which Brodie<sup>2</sup> had already formerly observed. Carbon dioxide, under a pressure of 3–10 mm. mercury, splits up very rapidly and up to 70 per cent. into carbon monoxide and oxygen (Norman Collie<sup>3</sup>).

Carbonic acid, in the presence of water, is converted into formic acid and oxygen (Losanitsch and Jovitschitsch<sup>4</sup>); the latter, partially ozonized, produces hydrogen peroxide.

Löb<sup>5</sup> showed that moist carbon dioxide also always yields carbon monoxide and only the latter forms the starting point for formic acid. The following reactions occur:

1.  $2 CO_2 = 2 CO + O_2$ ,
2.  $CO + H_2O = HCOOH$ ,
3.  $3 O_2 = 2 O_3$ ,
4.  $H_2O + O_3 = H_2O_2 + O_2$ .

<sup>1</sup> Essai de Mécanique chimique II, 377 (1879).

<sup>2</sup> London R. Soc. Proceed. **21**, 245 (1873); Lieb. Ann. **169**, 270 (1873).

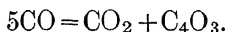
<sup>3</sup> Journ. of the Chem. Soc. **465**, 1063 (1901).

<sup>4</sup> Ber. d. deutsch. chem. Gesellsch. **30**, 135 (1879).

<sup>5</sup> Sitzungsberichte d. niederrheinischen Gesellschaft für Natur- u. Heilkunde (1903).

Carbonic acid and hydrogen, according to the experiments of Losanitsch and Jovitschitsch,<sup>1</sup> also unite to form formic acid.

**Carbon Monoxide.**—Considering the easy decomposability of carbonic acid with splitting off of carbon monoxide, the latter's behavior is particularly interesting. According to Berthelot<sup>2</sup> it breaks up into carbonic acid and the above-mentioned suboxide:



Moist carbon monoxide, according to the concordant results of Losanitsch<sup>1</sup> and Jovitschitsch, of Löb<sup>3</sup>, and of Hemptinne,<sup>4</sup> yields formic acid. There are also always formed some carbonic acid (Maquenne,<sup>5</sup> and Hemptinne) and hydrogen (Maquenne). The dimensions of the "electrizer," particularly the distance of the walls between which the discharge occurs, are of special influence on the result (Hemptinne).

The influence of the experimental conditions is shown in the action of the silent discharge upon a mixture of carbon monoxide and hydrogen. Thénard, Brodie, and Berthelot<sup>6</sup> found a solid body  $(\text{C}_4\text{H}_3\text{O}_3)_n$ ; Berthelot also observed a little carbon dioxide, acetylene, and an olefine-like hydrocarbon. Losanitsch and Jovitschitsch<sup>7</sup> obtained formaldehyde and its polymers; Hemptinne observed an oily liquid, without being able to say anything definite regarding the formation of formaldehyde.

At any rate all these experiments are worthy of the most thorough study. If the assertion of Phipson<sup>8</sup> is correct, that in plants hydrogen peroxide first produces formaldehyde from the carbonic acid  $(\text{CO}_2 + \text{H}_2\text{O}_2 = \text{CH}_2\text{O} + \text{O}_3)$ , the possibility of

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<sup>1</sup> l. c.

<sup>2</sup> Essai de Mécanique chimique II, 379 (1879).

<sup>3</sup> See note 5 on page 266.

<sup>4</sup> Bull. de l'Acad. roy. de Belg. [3] **34**, 269 (1897).

<sup>5</sup> Bull. soc. chim. [2] **39**, 308 (1883).

<sup>6</sup> Essai de Mécanique chimique II, 382 (1879).

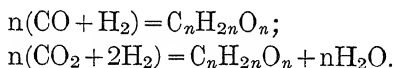
<sup>7</sup> l. c.

<sup>8</sup> Chem. News, **50**, 37, 288 (1884).

the formation of sugar by polymerization is at once given. The well-known Bayer theory, of the formation of sugar in plants, in connection with the above-mentioned view of Berthelot on the importance of atmospheric tensions for the chemical reactions of plants thus obtains new essential, and experimentally accessible, facts.

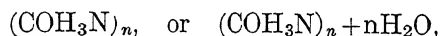
Recent investigations of Berthelot<sup>1</sup> deserve the greatest attention exactly in this connection. He found:

1. Carbon monoxide and carbon dioxide condense with an excess of hydrogen to carbohydrates:



2. If only a little hydrogen is present, complicated compounds rich in oxygen result.

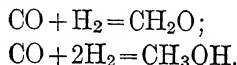
3. In a mixture of carbon monoxide, carbon dioxide, hydrogen, and nitrogen, the discharge produces nitrogen containing compounds having the formula:



which are comparable with hydrocyanic acid, and the compounds of the carbamide and xanthine groups.

With an excess of carbon monoxide Berthelot finds substances which seem related to parabanic acid. If water occurs in the reactions, ammonium nitrite is present.

Berthelot's observations are confirmed by the experiments of A. Slosse,<sup>2</sup> who, by subjecting a mixture of 1 volume carbon monoxide and 2 volumes hydrogen to the induction action in an ozonizer, obtained a crystalline, fermentable sugar which could have been formed from formaldehyde and methyl alcohol—both of which can be shown to be present—by the further action of the discharge:



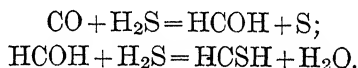
<sup>1</sup> Compt. rend. **126**, 609 (1898).

<sup>2</sup> Bull. de l'Acad. roy. de Belg. **35**, 547 (1898).

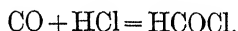
Berthelot has published a paper<sup>1</sup> on the apparatus employed in his experiments, the methods of the quantitative determinations, the influence of the conditions on the reaction velocity, and the dependence of the results upon the duration of the experiment. The latter is particularly important for the theoretical interpretation of the results. Simple, binary compounds are primarily formed which are secondarily polymerized to complex compounds—similarly as in physiological processes, in which the assimilated substances, after being split up into simpler substances for the purpose of nutrition, are again united to complicated compounds.<sup>2</sup>

Losanitsch and Jovitschitsch,<sup>3</sup> by the action of the silent electric discharge upon a mixture of carbon monoxide with other gases, have also accomplished the following syntheses. They obtained:

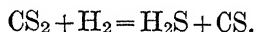
1. From *carbon monoxide* and *hydrogen sulphide*: Formaldehyde and sulphur, and thioformaldehyde and its polymers respectively, besides water,



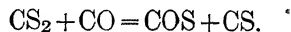
2. From *carbon monoxide* and *hydrochloric acid*: The unstable formylchloride:



3. From *carbon disulphide* and *hydrogen*: Hydrogen sulphide and carbon monosulphide:



4. From *hydrogen sulphide* and *carbon monoxide*: Carbon oxysulphide and carbon monosulphide:



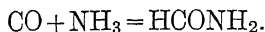
<sup>1</sup> Compt. rend. **126**, 561 (1898); **131**, 772 (1900).

<sup>2</sup> l. c.

<sup>3</sup> Ber. d. deutsch. chem. Gesellsch. **30**, 135 (1897).

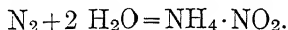


5. From *carbon monoxide* and *ammonia*: Formamide:



According to Slosse,<sup>1</sup> 1 vol. CO and 2 vols. NH<sub>3</sub> give a crystalline substance resembling urea.

6. From *nitrogen* and *water*: Ammonium nitrite:



In the further description of the results obtained in the realm of silent discharges we will first consider the behavior of single organic substances, then that of mixtures.

## II. *Hydrocarbons.*

**Methane.**—Aliphatic hydrocarbons, exposed to the action of a high-tension discharge, yield hydrogen, a little acetylene, which in the course of the experiment can again disappear by polymerization, and polymerized hydrocarbons. From methane Berthelot<sup>2</sup> obtained the last-mentioned gases, a resinous hydrocarbon, and traces of a fluid possessing a turpentine odor. He found—in percentages by volume—from 100 CH<sub>4</sub>: 105.2 H<sub>2</sub>, 4.4 CH<sub>4</sub>, a solid hydrocarbon of the empirical formula C<sub>10</sub>H<sub>18</sub>.

*Methane* and *oxygen*, according to Maquenne,<sup>3</sup> yield formaldehyde besides considerable formic acid.

*Methane* and *carbon monoxide*, according to Losanitsch and Jovitschitsch,<sup>4</sup> unite to acetaldehyde and its condensation and polymerization products; according to Hemptinne,<sup>5</sup> aldehydic substances.

*Methane* and *carbonic acid* condense (Thénard and Berthelot<sup>2</sup>) to an insoluble carbohydrate; Berthelot observed the presence of a trace of butyric acid. The residual gases contained a little acetylene and considerable carbon monoxide.

<sup>1</sup> Bull. de l'Acad. roy. de Belg. **35**, 547 (1898).

<sup>2</sup> Compt. rend. **82**, 1360 (1876); *Traité de Mécanique Chimique* II, 379 (1879). See also Compt. rend. **126**, 561 (1898).

<sup>3</sup> Bull. soc. chim. **37**, 298 (1882).

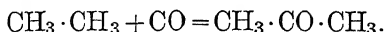
<sup>4</sup> Ber. d. deutsch. chem. Gesellsch. **30**, 135 (1897).

<sup>5</sup> Bull. de l'Acad. roy. de Belg. [3] **34**, 275 (1897).

*Methane and nitrogen* in the mixture 100 CH<sub>4</sub> + 100 N<sub>2</sub> give 117.7 H<sub>2</sub>, 3.4 CH<sub>4</sub>, 74 N<sub>2</sub>, and a solid body having approximately the composition, C<sub>8</sub>H<sub>12</sub>N<sub>4</sub> (Berthelot<sup>1</sup>).

**Ethane.**—From pure ethane Berthelot, at the beginning of the experiment, obtained (l. c.) a little acetylene and ethylene besides a resinous hydrocarbon. He found at the end of the experiment, from 100 C<sub>2</sub>H<sub>4</sub>: 107.8 H<sub>2</sub>, 0.7 CH<sub>4</sub>, C<sub>10</sub>H<sub>18</sub>. The unsaturated hydrocarbons had become polymerized.

*Ethane and carbon monoxide* yielded Hemptinne (l. c.) chiefly acetaldehyde, also some acetone:



*Ethane and nitrogen.*—There were obtained from 100 C<sub>2</sub>H<sub>6</sub> + 100 N<sub>2</sub> (Berthelot): 98.2 H<sub>2</sub>, 3.0 CH<sub>4</sub>, 73.5 N<sub>2</sub>, C<sub>16</sub>H<sub>32</sub>N<sub>4</sub>.

**Ethylene.**—100 C<sub>2</sub>H<sub>4</sub> gave 25.15 H<sub>2</sub>, 4.35 C<sub>2</sub>H<sub>6</sub> (C<sub>8</sub>H<sub>14</sub>)<sub>n</sub> (Berthelot). In former experiments Berthelot had obtained a fluid (C<sub>20</sub>H<sub>16.6</sub>) already observed by Thénard.

*Ethylene and nitrogen.*—100 C<sub>2</sub>H<sub>4</sub> + 100 N<sub>2</sub> gave 28.6 H<sub>2</sub>, 0.4 C<sub>2</sub>H<sub>6</sub>, 62.2 N<sub>2</sub>, C<sub>16</sub>H<sub>32</sub>N<sub>4</sub>.

**Propylene.**—100 parts yielded: 34.2 H<sub>2</sub>, 0.7 CH<sub>4</sub>, C<sub>15</sub>H<sub>26</sub>.

*Propylene and nitrogen.*—100 C<sub>3</sub>H<sub>6</sub> + 100 N<sub>2</sub> gave 17.8 H<sub>2</sub>, 60.5 N<sub>2</sub>, C<sub>15</sub>H<sub>28</sub>N<sub>4</sub>.

**Trimethylene.**—100 C<sub>3</sub>H<sub>6</sub> → 37.3 H<sub>2</sub>, 1.4 CH<sub>4</sub>, C<sub>15</sub>H<sub>26</sub>.

*Trimethylene and nitrogen.*—100 C<sub>3</sub>H<sub>6</sub> + 100 N<sub>2</sub> → 41.4 H<sub>2</sub>, 1.6 CH<sub>4</sub>, 61.4 N<sub>2</sub>, C<sub>15</sub>H<sub>26</sub>N<sub>4</sub>.

**Acetylene.**—100 C<sub>2</sub>H<sub>2</sub> → 1.8 H<sub>2</sub>, 0.8 C<sub>2</sub>H<sub>4</sub>, 0.08 C<sub>2</sub>H<sub>6</sub>, and an explosive substance. In the presence of hydrogen this substance is partially absorbed by the acetylene.

*Acetylene and nitrogen.*—100 C<sub>2</sub>H<sub>2</sub> + 100 N<sub>2</sub> gave no hydrogen and no hydrocarbon, but 88.6 N<sub>2</sub> and a solid substance, C<sub>16</sub>H<sub>16</sub>N<sub>2</sub>.

**Allylene.**—100 C<sub>3</sub>H<sub>4</sub> → 3 H<sub>2</sub>, (C<sub>15</sub>H<sub>19</sub>)<sub>2</sub>.

*Allylene and nitrogen.*—100 C<sub>3</sub>H<sub>4</sub> + 100 H<sub>2</sub> → 82.2 N<sub>2</sub>, C<sub>15</sub>H<sub>20</sub>N<sub>2</sub>.

In the experiments of Berthelot the gas analyses refer to the residual gas volume after the discharge has acted on the

<sup>1</sup> Compt. rend. 126, 567 (1898).

gaseous mixture for 24 hours. The high molecular formulæ give approximately the composition of the solid condensation products.

Berthelot<sup>1</sup> thus summarizes his experiences as to these reactions:

1. The limit hydrocarbons  $C_nH_{2n+2}$  lose 2 atoms of hydrogen per molecule. Solid hydrocarbons, most probably of a cyclical nature, are formed as polymerization products.

2. The olefines  $C_nH_{2n}$  also polymerize with loss of hydrogen. The solid products hereby formed,  $(C_nH_{2n})_m - H_2$ , in which  $m$  equals 4 or 5, or a multiple of these values, remind one of the camphenes, so far as their composition is concerned. They certainly belong to the cyclical hydrocarbons.

3. The acetylene hydrocarbons,  $C_nH_{2n-2}$ , polymerize without loss of hydrogen.

4. All hydrocarbons take up nitrogen, forming probably cyclical polyamines; methane and ethylene hydrocarbons seem to give tetramines; and acetylene hydrocarbons, diamines.

**Benzene** gave Hemptinne<sup>2</sup> resinous substances, several hydrocarbons, a little acetylene, and hydrogen.

*Benzene* and *hydrogen* easily unite under the influence of the discharge. Berthelot<sup>3</sup> found that 1 cc. benzene takes up 250 cc. hydrogen, i.e., about 2 equivalents, forming a solid polymeric hydrocarbon  $(C_6H_8)_n$ .

*Benzene* and *nitrogen*, according to Berthelot,<sup>4</sup> form a polymeric condensation product, one part by weight of benzene taking up about 0.12 part by weight of nitrogen. The substance, on being heated, splits off ammonia and seems to be a diphenylenediamine. Recently Berthelot<sup>5</sup> has found that *argon* is also absorbed by aromatic compounds, especially by mercury phenide, forming a mercurargon phenide. Mercury methide, on the contrary, does not absorb argon, but if nitrogen

<sup>1</sup> See also Jahrb. d. Elektrochemie of Nernst and Borchers, V, 202 et seq. (1899).

<sup>2</sup> Ztschr. f. phys. Chemie 25, 298 (1898)

<sup>3</sup> Compt. rend. 82, 1360 (1876).

<sup>4</sup> Ann. chim. phys. 11, 35 (1897).

<sup>5</sup> Compt. rend. 129, 71, 378 (1899).

is simultaneously present, it condenses with this to a condensation product of approximately the formula  $C_{20}H_{34}N_5$ .

**Turpentine** ( $C_{20}H_{16}$ ) unites with about 2.5 equivalents of hydrogen to a solid polymeric body.<sup>1</sup>

### III. Alcohols.

**Methyl Alcohol.**—According to Maquenne,<sup>2</sup> the vapor of methyl alcohol is decomposed by the silent discharge chiefly into methane and carbon monoxide; some hydrogen, ethylene, and acetylene and very little carbonic acid, are also produced. The quantity of hydrogen increases with increasing pressure (from 3–100 mm. mercury pressure), that of the other products decreases:

Pressure. .	3 mm.	100 mm.
CO. ....	24.3	19.6
CO <sub>2</sub> ....	0.0	0.0
C <sub>2</sub> H <sub>2</sub> + C <sub>2</sub> H <sub>4</sub> ....	4.3	0.9
C <sub>2</sub> H <sub>4</sub> ....	51.0	36.7
H <sub>2</sub> ....	20.4	42.8

A decomposition is caused by a high temperature similar to that produced by the discharge.

A. Hemptinne subjected a large number of substances to rapid electric oscillations in an arrangement which, according to the method of Lecher,<sup>3</sup> permitted an investigation of the influence of various wave lengths.<sup>4</sup> He found that methyl alcohol<sup>5</sup> at 15 mm. pressure and with weak oscillations gave:

Undecomposed alcohol. ....	2.0%
Carbonic acid. ....	4.2%
Carbon monoxide. ....	30.4%
Hydrogen. ....	30.5%
Methane (and other hydrocarbons). . .	32.9%

<sup>1</sup> *Traité de Mécanique chimique* II, 382 (1879).

<sup>2</sup> *Bull. soc. chim.* [2] **37**, 298 (1882); **40**, 60 (1883).

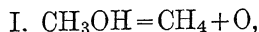
<sup>3</sup> *Wied. Ann.* **41**, 850 (1890).

<sup>4</sup> *Ztschr. f. phys. Chem.* **22**, 358 (1897).

<sup>5</sup> *Ibid.* **25**, 284 (1898).

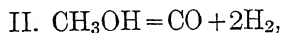
Stronger oscillations produced about the same effects.

Hemptinne suggests the following three problematical equations for explaining the reaction:

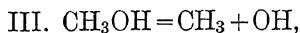


the oxygen acts in turn upon the methane and forms  $\text{CO}_2$ ,  $\text{CO}$ , and  $\text{H}_2\text{O}$ , while methane itself simultaneously breaks up into hydrogen and other hydrocarbons.

The following processes seem to him less likely:

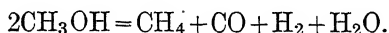


because the solid reaction product of hydrogen and carbon monoxide, which Berthelot found, is not present, and:



with subsequent polymerization, since here the formation of large quantities of methane is difficult to explain.

Owing to the present existing difficulty of explaining the complex action of electric oscillations, I should like to here refer, but only by way of suggestion, to a further possibility which takes account of the polymerizing influence of the oscillations. It is imaginable that primarily two or several molecules of methyl alcohol become associated and yield a product which is broken up during the progress of the experiment. The decomposition products thus formed are then further effected by the influence of the oscillations. The total equation would then be the following:



As some carbon dioxide is always formed from carbon monoxide and water, such a breaking up of the molecules would agree with the analytical results of Hemptinne.

**Ethyl Alcohol.**—Maquenne<sup>1</sup> obtained a gas which possessed

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<sup>1</sup> Bull. soc. chim. [2] 37, 298 (1882); 40, 61 (1883).

a strong aldehydic odor, and contained hydrogen, ethane, ethylene, acetylene, carbon monoxide, and carbon dioxide. He determined the following results for various pressures:

Pressure.	2 mm.	110 mm.
CO <sub>2</sub> .....	2.2	0.0
CO.....	11.0	} 14.8
C <sub>2</sub> H <sub>2</sub> + C <sub>2</sub> H <sub>4</sub> .....	14.0	
C <sub>2</sub> H <sub>6</sub> .....	30.1	
H <sub>2</sub> .....	42.6	
		65.4

Hemptinne<sup>1</sup> found:

Undecomposed alcohol.....	3%
Carbon dioxide.....	2%
“ monoxide.....	22%
Hydrogen.....	25%
Ethane and methane.....	48%

To prove the supposition of a decomposition:  $C_2H_5OH = C_2H_6 + O$ , Hemptinne added some phosphorus to the vapors, for immediately binding the oxygen occurring intermediately. He actually found a decrease in carbon monoxide and the hydrocarbons and a considerable increase in the quantity of hydrogen. Carbon dioxide was not present. On the contrary, if oxygen is added directly to the alcohol vapor, the quantities of carbon mon- and dioxide and of the hydrocarbons increase considerably, while the quantity of hydrogen decreases. These phenomena, of course, do not prove the primary process,  $C_2H_5OH = C_2H_6 + O$ , which is altogether unlikely. For the chief change occurs in the proportion of hydrogen to hydrocarbon (without P: 20% H<sub>2</sub>, 62.5% C<sub>2</sub>H<sub>6</sub> + CH<sub>4</sub>; with P: 65% H<sub>2</sub>, 27% C<sub>2</sub>H<sub>6</sub> + CH<sub>4</sub>); it points to the influence of the medium upon the reaction velocity and the equilibrium, but does not permit a decision as to the course of the reaction. The explanation of these processes occurring with simple substances still requires a great deal of experimental work.

Absolute, fluid alcohol, according to Berthelot,<sup>1</sup> breaks up slowly with evolution of hydrogen and ethane. Aldehyde is simultaneously produced and a complex hydrocarbon having perhaps the composition  $C_nH_{2n}$ .

Hemptinne<sup>2</sup> also investigated the following alcohols:

**Propyl Alcohol.**—Result:

Undecomposed alcohol. . . . .	2%
Carbon monoxide. . . . .	16%
Hydrogen. . . . .	37%
Propane, ethane, and methane. . . . .	45%

**Isopropyl Alcohol** breaks up, under similar conditions, in almost exactly the same way as the normal alcohol.

**Allyl Alcohol** was exposed for only a minute to electric oscillations; it yielded:

Undecomposed alcohol. . . . .	35%
Hydrocarbons, $C_nH_{2n}$ . . . . .	35%
Carbon monoxide. . . . .	10%
Hydrogen, and other hydrocarbons. . . . .	20%

**Glycerin.**—The gaseous products formed are carbon dioxide, carbon monoxide, and hydrogen.

**Glycol** gives carbon dioxide, carbon monoxide, hydrogen, and methane.

**Phenol** is decomposed, splitting off a gas composed of carbon mon- and dioxide and hydrogen.

#### IV. Aldehydes and Ketones.

Aldehydes and ketones were also investigated by Hemptinne.<sup>2</sup>

**Acetaldehyde** gives carbon monoxide, hydrogen, and methane.

**Paraldehyde.**—The gaseous products formed are carbonic acid,

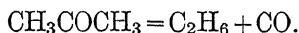
<sup>1</sup> Compt. rend. 126, 693 (1898).

<sup>2</sup> l. c.

hydrocarbons ( $C_nH_{2n}$ ), carbon monoxide, hydrogen, and methane.

**Propylaldehyde** breaks up in a different manner than the isomeric allyl alcohol. The gas, separated from the aldehyde, contained carbonic acid, methane, and ethane, hydrocarbons,  $C_nH_{2n}$ , carbon monoxide, and hydrogen.

**Acetone**, likewise isomeric with allyl alcohol, gives the same products as propyl aldehyde. As the quantity of carbon monoxide does not decrease in the presence of phosphorus, Hempinne concludes that the following decomposition process occurs:



According to Maquenne<sup>1</sup> acetone vapor is decomposed by the electric discharge into hydrogen, ethane, and carbon monoxide, a small quantity of acetylene and carbon dioxide being also formed. The quantity ratios are less dependent upon the pressure than in the case of methyl and ethyl alcohol:

Pressure.	Trifling.	100 mm.
CO <sub>2</sub> .....	1.1	0.6
CO.....	37.5	42.1
C <sub>2</sub> H <sub>4</sub> .....	4.3	2.9
C <sub>2</sub> H <sub>6</sub> .....	32.4	30.0
H <sub>2</sub> .....	24.7	24.4

**Glyoxal** breaks up into carbonic acid, hydrocarbons ( $C_nH_{2n}$ ), and hydrogen.

#### V. Acids and Esters.

**Formic Acid.**—Maquenne<sup>2</sup> has investigated the action of the discharge upon formic-acid vapor under various pressures. He found carbon monoxide, carbonic acid, and hydrogen. With increasing pressure (2–100 mm. mercury) the quantity of carbon monoxide decreases, while the quantities of carbonic

<sup>1</sup> Bull. soc. chim. [2] 40, 63 (1883).

<sup>2</sup> Ibid. 39, 306 (1883).



acid and hydrogen increase correspondingly. Hemptinne<sup>1</sup> obtained similar results.

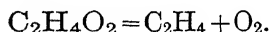
*Formic Methyl Ester* yielded the following gases (Maquenne<sup>2</sup>):

Carbon dioxide. . . . .	8.1%
“ monoxide. . . . .	46.8%
Ethylene. . . . .	0.5%
Methane. . . . .	20.6%
Hydrogen. . . . .	24.0%

*Formic Ethyl Ester* gives (Hemptinne):

Carbon dioxide. . . . .	13%
“ monoxide. . . . .	42%
Hydrogen. . . . .	25%
Ethane and methane. . . . .	20%

**Acetic Acid.**—Besides hydrogen, carbon mon- and dioxides, Maquenne<sup>3</sup> also obtained methane, ethylene, and acetylene. With increasing pressure he found an increase in hydrogen and carbon monoxide, a decrease in carbonic acid and hydrocarbons. Hemptinne observed similar results with his experimental arrangement. He accepts the following as the primary decomposition process, corresponding to that of the alcohols:



Hemptinne does this to explain the presence of large quantities of ethylene.

**Acetic Methyl Ester**, according to Hemptinne, breaks up quantitatively almost in the same manner as the isomeric formic ethyl ester:

Carbon dioxide. . . . .	11%
“ monoxide. . . . .	47%
Hydrogen. . . . .	20%
Ethane and methane. . . . .	22%

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<sup>1</sup> l. c.

<sup>2</sup> Bull. soc. chim. [2] 40, 64 (1883).

<sup>3</sup> Ibid. 39, 306 (1883).

**Propionic Acid** gives carbonic acid, hydrocarbons ( $C_nH_{2n}$ ), carbon monoxide, hydrogen, and saturated hydrocarbons.

**Glyceric Acid.**—Although glycerin did not yield any hydrocarbons, there were obtained, on using glyceric acid, besides carbon mon- and dioxides and hydrogen, about 20% methane.

**Glycollic Acid.**—This acid,  $CH_2OHCOOH$ , breaks up smoothly into hydrogen (70%) and carbonic acid (30%).

**Oxalic Acid** splits off carbonic acid, carbon monoxide, and hydrogen.

**Benzoic Acid** gives the same products. Hemptinne, who has investigated the last-mentioned acids, draws the conclusion from his observations that the molecule is burst by the influence of the electric vibrations, whereby isomeric substances often give the same bodies, and sometimes various decomposition products.

#### VI. *Concerning the Binding of Nitrogen to Organic Substances.*

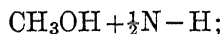
(Berthelot's Investigations.)

##### Alcohols and Nitrogen.<sup>1</sup>

Berthelot subjected weighed quantities of the alcohols and certain volumes of nitrogen to the action of the silent electric discharge. In most cases the action was limited to 24 hours (when it was continued for a longer period, an absorption of nitrogen no longer occurred). He obtained the following results

**Methyl Alcohol.**—0.0515 g. and 11.5 cc.  $N_2$  were used. Composition of the resulting gas:  $H_2=18.5$  cc.,  $CO=0.9$  cc., absorbed nitrogen: 9.4 cc.

These values correspond to the process:

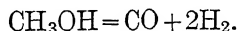
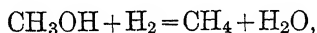


a body of the composition  $C_4H_{12}N_2O_4$  or  $[C_2H(OH)NH_2 + H_2O]_2$  must therefore have been formed. This formula points to the formation of an amidine or its hydrate.

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<sup>1</sup> Compt. rend. 126, 616 (1898).

The alcohol is also decomposed by itself, which could be proved by experiments of short duration in which no notable absorption of nitrogen had taken place. According to the gas analyses, the decomposition of the alcohol occurs as shown in the equations:

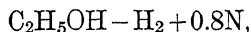


(Cf. the experiments of Hemptinne, p. 274.)

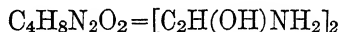
The other alcohols behave analogously.

**Ethyl Alcohol.**—There were employed 0.056 g. and 19.1 cc.  $\text{N}_2$ . Gas obtained:  $\text{H}_2 = 26.8$  cc.,  $\text{CO}_2 = 0.2$  cc.,  $\text{N}_2 = 8.2$  cc.; absorbed nitrogen, 10.9 cc.

These values represent the reaction

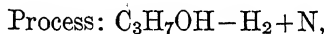


from which (taking into consideration the alcohol decomposed without absorption of nitrogen) the formation of an amidine of the formula

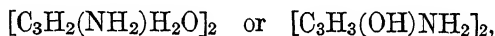


results.

**Normal Propyl Alcohol.**—Employed 0.082 g. and 19.6 cc. nitrogen. Gas obtained:  $\text{H}_2 = 23.4$  cc.,  $\text{CO}_2 = 2.0$  cc.,  $\text{CO} = 0.2$  cc.,  $\text{N}_2 = 7.4$  cc.; absorbed nitrogen, 12.2 cc.



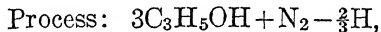
from which the formation of the amidine,



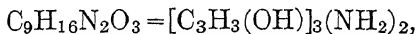
is inferred.

**Isopropyl Alcohol** shows the same ratios as the normal alcohol.

**Allyl Alcohol.**—Employed: 0.150 g. and 23.5 cc.  $N_2$ .  
Residual gas:  $H_2=6.8$  cc.,  $N_2=4.3$  cc. Absorbed nitrogen,  
19.2 cc.



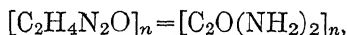
from which is inferred the formation of the amidine,



**Phenol** and **pyrocatechin** readily absorb nitrogen; *pyrogallol*,  
*hydroquinone*, and *resorcin* absorb the gas quite slowly.

#### Ethers and Nitrogen.<sup>1</sup>

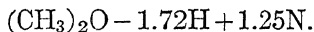
**Ethylene Oxide.**—100 cc.  $C_2H_4O$  and 115.5 cc.  $N_2$  give:  
 $H_2=5.5$  cc.,  $C_2H_6=0.4$  cc.,  $N_2=10.1$  cc. Absorbed nitrogen  
105.9 c.c. The formation of a body,



is inferred; it could be considered as an isomer of a hydrate  
of cyanamide.

**Methyl Ether.**—100 cc.  $(CH_3)_2O$  and 127.9 cc.  $N_2$  give:  
 $H_2=86$  cc.,  $N_2=65.6$  cc. Absorbed nitrogen: 62.3 cc.

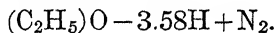
The ratio of the elements which react is the following:



The proportions are similar to those of the isomeric ethyl alcohol, but in the case of methyl ether they indicate a mixture.

**Ethyl Ether.**—100 cc.  $(C_2H_5)_2O$  and 141 cc.  $N_2$  give:  
 $H_2=174.2$  cc.,  $N_2=44.6$  cc. Absorbed nitrogen: 96.4 cc.

Ratio of the reacting elements:

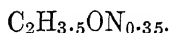


Ethyl ether therefore gives off twice as much hydrogen and absorbs twice as much nitrogen as methyl ether, which seems to point to a fixed ratio between the nitrogen compounds formed and the molecular weight of the compounds started with.

Aldehydes, Ketones, and Nitrogen.<sup>1</sup>

**Acetaldehyde.**—Employed: 24 cc.  $\text{CH}_3\text{CHO}$  and 22.8 cc.  $\text{N}_2$ . Based on 100 cc. aldehyde, there were obtained at the end of the reaction:  $\text{H}_2=25.8$  cc.,  $\text{H}_2=59.6$  cc. Absorbed nitrogen: 35.4 cc.

The ratio of the reacting elements is expressed by the formula



The ratio also remains constant with an excess of nitrogen, and leads to the reaction product



which, judging from its marked basic character, seems to contain amido-groups.

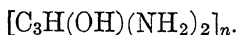
Ethylene oxide, isomeric with this aldehyde, combines with five times as much nitrogen.

**Propyl Aldehyde.**—A large excess of nitrogen being present, there were formed, based on 100 cc.  $\text{C}_2\text{H}_5\text{CHO}$  vapor:  $\text{H}_2=43.6$  cc.,  $\text{CO}_2+\text{CO}=4$  cc. Absorbed nitrogen: 66.7 cc.

These quantities correspond to a product  $\text{C}_9\text{H}_{16}\text{N}_4\text{O}_3$ , in which there are likewise supposed to be several amido-groups.

**Acetone.**—By employing an excess of nitrogen, there were formed, based upon 100 cc.  $\text{CH}_3\text{COCH}_3$  vapor:  $\text{H}_2=33.3$  cc. Absorbed nitrogen: 89 cc.

These relations are expressed by the formula

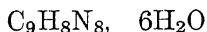


Allyl alcohol, which is isomeric with acetone, absorbs only one third as much nitrogen as acetone takes up and only half that taken up by propyl aldehyde.

**Methylal.**—With an excess of nitrogen there are formed from 100 cc.  $\text{CH}_2(\text{OCH}_3)_2$ :  $\text{H}_2=71.1$  cc.,  $\text{CO}_2=4.4$  cc.,  $\text{CO}=2.2$  cc. Absorbed nitrogen: 128.9 cc.

<sup>1</sup> Compt. rend. 126, 671 (1898).

Berthelot seems to refer the calculated composition of the reduction product



to polyamines having many hydroxyl groups and derived from the type  $(\text{CHN})_n$ , i.e., bodies which were obtained by him from carbon monoxide, hydrogen, and nitrogen by means of the silent electric discharge.

The following experiments could not be carried out to the end of the reaction on account of the trifling vapor tension of the materials started with.

**Aldol** takes up large quantities of nitrogen, giving off trifling amounts of hydrogen; *paraldehyde* behaves similarly. *Trioxymethylene*, on the contrary, and *formaldehyde* solution absorb nitrogen only very slowly.

**Camphor** takes up nitrogen, forming a basic body.

**Benzaldehyde, benzoïn, cinnamic aldehyde, salicylic aldehyde, furfural, and quinone**, under the influence of the discharge, absorb nitrogen more or less rapidly.

**Glucose, cellulose (paper), and dextrine**<sup>1</sup> can slowly take up nitrogen; likewise the humus substances obtained by the action of concentrated hydrochloric acid upon sugar.

#### Acids and Nitrogen.<sup>2</sup>

**Formic Acid.**—Since formic acid is easily split up by the silent electric discharge into carbon mon- and dioxides and hydrogen, a noticeable absorption of nitrogen does not occur, but *formic methyl ester*, although being likewise fundamentally broken up, takes up larger quantities of nitrogen.

**Acetic Acid.**—This acid absorbs nitrogen, forming trifling quantities of ammonia and a product which, according to the analyses of the gases obtained by the discharge, is said to have the composition of an amine or amide (Berthelot). The behavior of *acetic methyl ester* gives results which call to mind

<sup>1</sup> Essai de Mécanique chimique II, 338 (1879).

<sup>2</sup> Compt. rend. 126, 681 (1898).

those of acetic acid and methyl alcohol when each substance is subjected by itself to reaction with nitrogen.

Other acids investigated were:

**Propionic acid, crotonic acid, benzoic acid, succinic acid, maleic and fumaric acid, phthalic acid, camphoric acid, glycollic acid, lactic acid, malic acid, tartaric acid, the oxybenzoic acids, pyroracemic acid, lævulinic acid, dehydracetic acid, and acetoacetic acid (or its esters).**

All these substances (with the exception of fumaric and phthalic acid, which, under the experimental conditions, do not absorb nitrogen) take up more or less readily varying quantities of nitrogen. The m-oxybenzoic acid absorbs considerably less easily than its isomers.

#### Nitrogen Compounds and Nitrogen.<sup>1</sup>

**Methylamine.**—Hydrogen and nitrogen are split off, a solid product with alkaline reaction, and probably possessing the composition of hexamethylenetetramine, being formed.

**Dimethylamine** absorbs nitrogen, splitting off water in ratios that likewise indicate the formation of hexamethylenetetramine.

**Trimethylamine.**—This substance, by absorbing a correspondingly greater quantity of nitrogen, also seems to lead to the same compound.

**Ethylamine** does not react with nitrogen, but it gives off a quantity of hydrogen which indicates the formation of a body homologous to hexamethylenetetramine.

**Normal Propylamine** absorbs nitrogen and gives off hydrogen. The course of the reaction indicates the formation of tetramines, which are derived from methyl- and ethylamine.

**Iso-Propylamine** shows the same behavior as the normal compound.

**Allylamine** develops hydrogen, but neither absorbs nor splits off nitrogen. The reaction product has a strong odor of piperidine and perhaps the composition  $C_9H_{15}N_3$  or  $C_{12}H_{20}N_4$ .

<sup>1</sup> Compt. rend. 126, 775 (1898).

**Aniline, Methylaniline, Benzylamine, the Toluidines, Pyridine, and Piperidine** take up nitrogen. Experimental, essential facts for determining the nature of the resulting products are lacking.

**Ethylenediamine.**—The volume of this compound is rapidly increased by the action of the silent electric discharge. Hydrogen is primarily developed, with some ammonia, nitrogen, and methane or ethane. Absorption of nitrogen and ammonia soon occurs, and hydrogen is split off. In the second stage the formation of condensation products (polyamines) presumably predominates, while in the first period the decomposition of the material started with prevails.

**Propylenediamine** behaves precisely like ethylenediamine.

**Phenylenediamine (m- and p-), Benzidine and Nicotine** absorb very little nitrogen.

**Acetamide and Glycocoll** absorb little nitrogen, and the quantity of the latter seems to depend upon the nitrogen absorption capacity of the respective acids.

**Sulphocarbamide** remains unchanged.

**Nitriles** (acetonitrile, benzonitrile, tolunitrile, benzyl cyanide) absorb nitrogen, the last three by direct addition without giving off another element, while acetonitrile gives hydrogen and some methane.

**Aldoxime** ( $\text{CH}_3 \cdot \text{CH} : \text{N} \cdot \text{OH}$ ) combines with nitrogen and splits off water.

**Phenylhydrazine** is slightly decomposed, splitting off hydrogen and nitrogen.

**Nitromethane** is fundamentally broken up, presumably by internal oxidation, and with formation of condensed products; hydrogen, oxygen, carbonic acid, and nitrogen are developed.

**Nitroethane**, unlike the last-mentioned compound, absorbs nitrogen. The behavior of nitromethane corresponds to that of formic acid, and that of nitroethane to that of acetic acid.

**Nitrobenzene** takes up little nitrogen.

The following substances were also investigated:

**Pyrrol, Indol, Indigotin, Azobenzene, and Albumens**, all absorbing nitrogen.



**Thiophene.**—This compound under the influence of the electric discharge absorbs as much as 8.6 per cent of its own weight of nitrogen,  $(C_4H_4S)_2N$  being formed (Berthelot).<sup>1</sup>

The following conclusions can be drawn from Berthelot's observations:

1. All the investigated alcohols fix nitrogen, forming amido-like substances.
2. The aliphatic alcohols thereby lose hydrogen (excepting allyl alcohol), an atom of nitrogen replacing a molecule of hydrogen.
3. The loss of hydrogen is related to the behavior of the hydrocarbons, which form the basis of the alcohols, when the former are subjected to the same conditions.
4. Phenols bind nitrogen in varying proportions, but without giving off hydrogen.
5. The isomeric aliphatic alcohols behave alike. They thus differ from the three dihydroxybenzenes.
6. All aldehydes bind nitrogen by forming condensation products. Amines or amides are produced. These are closely related to the ammonia derivatives of the aldehydes, particularly the glycosins, glyoxalines, and polyamines containing little hydrogen.
7. Organic acids, just like the alcohols, aldehydes, and hydrocarbons, generally combine with nitrogen, but no hydrogen, or but very little, is split off. Only phthalic acid and fumaric (contrary to maleic) acid do not absorb nitrogen.
8. Most of the investigated nitrogenous compounds absorb an additional quantity of nitrogen, and polyamines, polyamides, and condensation products seem to be produced. Exceptions, which do not show this behavior of absorbing nitrogen, are: ethylamine, allylamine, phenylhydrazine, sulphocarbamide, ethylenediamine, and propylenediamine. Methylamine and nitromethane even give off nitrogen; this is probably due to the low percentage of carbon.
9. Aliphatic nitrogen-containing compounds in taking up

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<sup>1</sup> Ann. chim. phys. **11**, 35 (1897).

nitrogen lose about as much hydrogen as their corresponding hydrocarbons and alcohols. Compounds are produced whose cyclic character becomes more pronounced with an increasing number of carbon atoms in the original molecules. Exceptions to this rule are compounds rich in oxygen, like nitroethane and glycocoll.

10. Cyclical compounds in absorbing nitrogen do not give off hydrogen any more than cyclical hydrocarbons and phenols. Piperidine, on the contrary, being a hydrated compound, loses hydrogen in absorbing nitrogen, just like aliphatic substances.

11. All compounds taking up nitrogen by simple addition—without giving off hydrogen—i.e., hydrocarbons, alcohols, aldehydes, acids, and bases, when subjected to the influence of the silent discharge, yield substances which behave like amides or amines. Since the formation of these substances cannot, of course, be based upon a substitution of  $\text{NH}_2$ ,  $\text{NH}$ , or  $\text{N}$  in place of hydrogen, we must ascribe cyclic constitutions to the products obtained.

12. The following table shows a comparison of polyamines formed from hydrocarbons, alcohols, and bases by reaction with nitrogen through the influence of the discharge. The formulæ of the reaction products are not rational ones, but merely arranged in such a way that the quantities of the separate elements in the molecule always refer to four nitrogen atoms. This is done to express, in a comparable manner, the atomic relations between the elements in the polyamines.

	Composition of Polyamines formed from				
	Hydrocarbons.	Alcohols.	Bases.		
			Primary.	Secondary.	Tertiary.
Methane Series	$\text{C}_8\text{H}_{12}\text{N}_4$	$\text{C}_8\text{H}_{16}\text{N}_4, 4\text{H}_2\text{O}$	$\text{C}_8\text{H}_{12}\text{N}_4$	$\text{C}_6\text{H}_{12}\text{N}_4$	$\text{C}_6\text{H}_{12}\text{N}_4$
Ethane Series	$\text{C}_{16}\text{H}_{32}\text{N}_4$	$\text{C}_8\text{H}_{16}\text{N}_4, 4\text{H}_2\text{O}$	$\text{C}_8\text{H}_{16}\text{N}_4$	$\text{C}_8\text{H}_{12}\text{N}_4$	
Propane Series	$\text{C}_{15}\text{H}_{28}\text{N}_4$	$\text{C}_{12}\text{H}_{16}\text{N}_4, 4\text{H}_2\text{O}$	$\text{C}_9\text{H}_{18}\text{N}_4$	$\text{C}_8\text{H}_{16}\text{N}_4$	
Allyl Series	$\text{C}_{30}\text{H}_{40}\text{N}_4$	$\text{C}_{18}\text{H}_{20}\text{N}_4, 6\text{H}_2\text{O}$	$\text{C}_{12}\text{H}_{20}\text{N}_4$		

The following relations result from the tables:

For an equal weight of nitrogen the condensation of the hydrocarbon residue combined with the nitrogen increases in the transition from derivatives of hydrocarbons to those of the alcohols, excepting the polyamines resulting from the methane series. This is very evident if the composition of the mentioned hydrocarbon residues is referred to an equal number of carbon atoms. The same increase is found if we pass from the derivatives of the alcohols to those of the primary bases; excepting the compounds of the ethane series. This condensation is twice as large with the products from diamines as with those from monamines.

## 2. BEHAVIOR OF VAPORS TOWARDS TESLA CURRENTS.

A few remarks may be made here concerning observations in a realm which promises to become especially important for theoretical organic chemistry. It has been known for some time that highly rarefied gases or vapors, when subjected to the action of highly tensioned electric vibrations, become luminous. Hemptinne,<sup>1</sup> by using Tesla currents and organic substances, has recently taken up the subject of the relation between luminosity and chemical action and the dependence of the phenomena upon the pressure. He found that the luminosity of the various substances in the arrangement of Tesla is dependent upon the pressure. A perceptible decomposition occurs from the beginning of the luminosity.

A connection exists between the pressure at which the light effects of organic substances begin and their molecular weights; but these relations have not yet been sufficiently explained.

H. Kaufmann<sup>2</sup> has made extensive investigations concern-

<sup>1</sup> Ztschr. f. phys. Chemie **22**, 358; **23**, 483 (1897); Bull. de l'Acad. roy. de Belg. **11**, 775 (1902).

<sup>2</sup> Ztschr. f. physik. Chem. **26**, 719 (1898); **27**, 519 (1898); **28**, 673 (1899); Ber. d. deutsch. chem. Gesellsch. **33**, 1725 (1900); **34**, 682 (1901); **35**, 473, 3668 (1902); **36**, 561 (1903).

ing the luminosity of organic vapors under the influence of Tesla currents at atmospheric pressure. He was thus enabled to formulate a series of remarkable laws.

His experiments were arranged in the following manner:

The electric field in which the vapors are excited to luminosity is produced by a Tesla transformer, on the inside of a somewhat wide test-tube which has been converted into an ozonizer. The outer layer, 5 cm. high and consisting of thin sheet copper, is wrapped half way up around the test-tube; the outer layer has a narrow vertical slit for conveniently observing the inside of the tube. The inner coat, of mercury or tin, is placed in a small, narrow glass tube, which is kept rigid and exactly in the axis of the test-tube by a stopper closing the latter. The stopper also supports a return-condenser arrangement, usually a rising tube. The substances to be investigated are placed in a solid or liquid state in the test-tube, and the whole tube is then filled with vapor by vigorous boiling.

Some unimportant changes in the arrangement, such as lowering the layers, etc., are made with very difficultly volatile substances and such that readily char.

The luminous phenomena in these ozonizers occur in the shape of more or less wide, colored bands of light, mostly in a horizontal and radial direction. Non-luminous vapors either remain wholly dark or become,—this is oftener the case,—interspersed with green-colored sparks. The sparks very rapidly decompose the vapors, precipitating carbonaceous substances; the luminosity itself, on the contrary, produces only extremely trifling changes in the substances.

The color of the luminous effects, in the majority of cases, is violet, with numerous gradations between blue and red, rarely yellow and green.

The hitherto observed regularities refer to the vapors emitting the first-mentioned colors. We shall emphasize only a few points among the great number of observations:

1. Aromatic substances usually possess an extraordinarily higher luminosity than aliphatic compounds. However, simple aromatic hydrocarbons like benzene, its homologues and benzene

derivatives, possessing two or more nuclei linked by aliphatic residues, are either non-luminous or only slightly so. But hydrocarbons containing two or more directly linked benzene nuclei like diphenyl, carbazol, and condensed nuclei like naphthalene, anthracene, and phenanthrene show a brilliant violet luminosity.

2. Substituents exert a powerful influence upon the light effects. The introduction of several hydroxyl groups into aromatic hydrocarbons of one nucleus produces luminous effects which do not occur with only one hydroxyl group in the molecule. The amino-group always excites luminosity even in mono-nuclear hydrocarbons. The effect of the amino-group often enforces that of the hydroxyl group, thus aminophenols produce luminous effects which are often very intense.

3. Acetyl, benzylidene, nitro-groups, the halogens, chlorine, and bromine, and the carboxyl group, on the contrary, considerably decrease the luminosity, sometimes completely.

Kaufmann seeks to employ these facts for obtaining an insight into the ring system of benzene. Instead of using the term "constitution," he uses that of "condition," and shows that in the luminous compounds the benzene nucleus is in an unstable condition, one in which it is disposed to change into a quinone-like structure. The condition of the benzene nucleus, determined by the chemical behavior of the ring, changes from substance to substance in the greatest variety. These conditions have possibilities which are represented by the Kekulé, the diagonal (Claus and Körner), and the Dewar formula with only one para-bond. The condition characterized in the first formula, according to Baeyer's investigations, is found in phloroglucin; the diagonal formula agrees excellently for phthalic acid; and the Dewar formula, for instance, for dimethyl-p-phenylenediamine.

The conditions for most of the benzene derivatives differ from these three limiting conditions and assume mostly an intermediate position which approximates more or less that of the one or other limiting condition.

The luminosity caused by the action of Tesla currents indicates that the ring of the respective substance exists in Dewar's condition; the stronger the luminosity the more pronounced the latter must be.

The one para-bond in Dewar's ring is unstable, and is characterized by the fact that it can easily be broken down, by oxidizers; it thus differs from the three para-bonds of the two other formulæ.

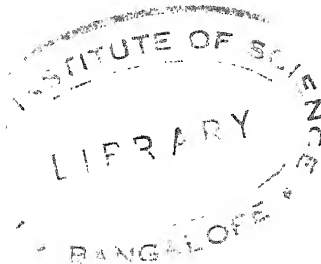
4. In the aliphatic series Tesla currents are absorbed and converted into light by the vapors of aldehydes and ketones; the carbonyl group is the sole carrier of the luminosity. The latter disappears with derivatives of aldehydes and ketones which do not have the carbonyl group. The luminosity decreases: Firstly, with increasing number of carbon atoms (introduction of methyl groups); secondly, with the entrance of a carboxethyl group; and thirdly, especially in the presence of a phenyl residue (benzaldehyde, acetophenone, etc., show no luminous effects). Ring ketones without a double bond between carbon atoms can be luminous; such with double bonds cannot.

Kaufmann explains the luminosity of aldehydes and ketones by the supposition that the carbonyl group, the carrier of the luminous effects in those substances, can occur in various states or conditions, like the benzene nucleus. Only such bodies which have the atoms of the carbonyl group loosely bound and in a reactive state can show luminosity. Reactability and luminosity run parallel. The latter is, hence, present in aldehydes and ketones, but not in acids, acid anhydrides, esters, and amides, all of which contain the same group but in a condition of extremely trifling reactability; or, we can say, the atoms of this group are firmly bound.

The luminosity of vapors under the influence of Tesla oscillations is undoubtedly closely related to the constitution of the substances. It also seems true that a continuous transition from the non-luminous to the luminous vapors takes place, so that only quantitative, but no substantial, differences exist between

the conditions characterized by the luminosity. In order to obtain a better understanding of the relations, it is necessary to measure these phenomena and, on the basis of quantitative determinations, to seek determinative connections, just as, for instance, has been done in the case of the conductivity of electrolytes.

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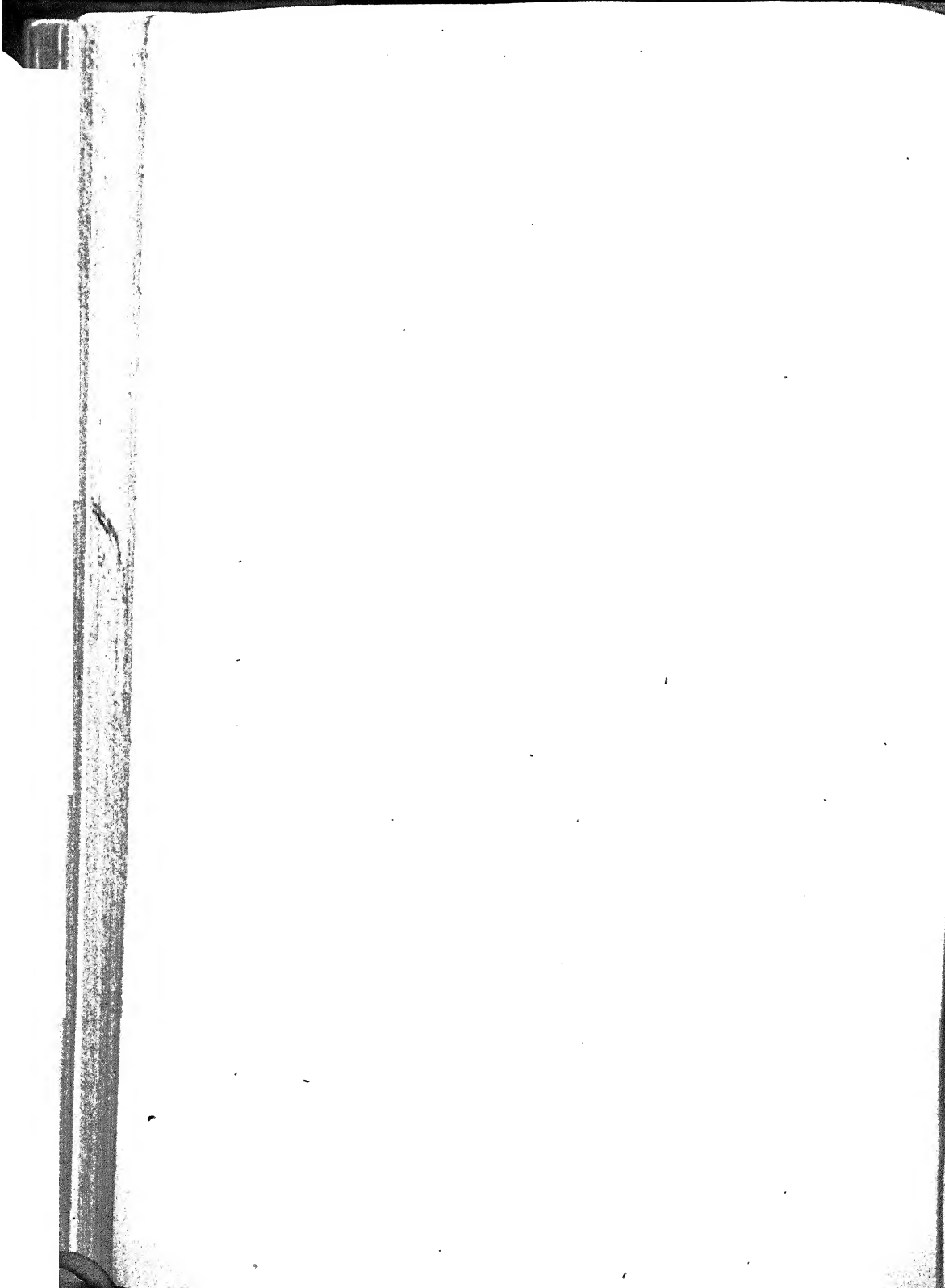
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